

MANUFACTURE OF BIOBASED MONOMERS AND VALUE-ADDED
PRODUCTS FROM SOYBEAN OIL

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ABSTRACT

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The depletion of non-renewable resources by modern societies and the need for a sustainable chemical industry are major factors that contribute to an increasing interest to study and develop new biobased polymers. The specific goal of this research was to study the synthesis of biobased polymer building blocks through ozonolysis of soybean-oil-based fatty acid methyl esters (FAMES), evaluate their purification feasibility by distillation and evaluate their potential for biobased polymer applications.

Ozonolysis reactions were conducted in two different solvent systems, in both batch and continuous reaction mode. In the first system, methanol was used both as solvent and esterification reagent, while sodium methoxide was added as the esterification catalyst. In the second system, water was used as solvent without catalyst addition. In the methanol system ozone oxidizes the double bonds of unsaturated FAMES, producing aldehydes (around 50% molar yield) and methyl esters (less than 15% molar yield). With dimethyl azelate as the target compound for biobased polyester building blocks, Oxone was used to convert the aldehydes into methyl esters, improving their molar yields to between 65% and 73%. In the water system, ozonolysis reactions yield aldehydes and carboxylic acids. The products from water system were also primarily aldehydes including hexanal, nonanal and methyl 9-oxononanoate with molar yields between 62% and 71%. For room temperature assays in a continuous system, the optimal flow rate for maximizing product

formation during ozonolysis in methanol system was found to be 15 ml/min (ratio of methanol to fame 2:1), while in water system was 40 ml/min (ratio of water to fame 3:1).

For purification of the ozonolysis products from both methanol and water systems, two distillation processes were designed and evaluated using simulation results. A fractional distillation was designed and simulated in Aspen Plus for products generated from the two systems, and most of the purity of products was above 0.99 with recoveries higher than 0.98. As some of the products are sensitive to temperature, an alternative distillation method was evaluated using wiped film distillation (WFD). This system was modeled using an equilibrium simulation with a flash separation module in Aspen Plus to predict the separation efficiency of multiple components. When the operating pressure in WFD is fixed, the study showed that modeling pressure in Aspen Plus is proportional to the pseudo bubble pressure of the mixture under the heating oil temperature of WFD. Since the WFD is similar to one-stage flash separation under a certain pressure, it is not recommended for separation of complex products with close relative volatility, like in the case of mixed products from ozonolysis of FAMES.

To evaluate the usage of biobased aldehydes for polymer applications, polyvinyl acetals were prepared during polymerization reactions of polyvinyl alcohol (PVOH) with three aldehydes generated from ozonolysis of FAMES in water system. Properties including decomposition temperature, glass transition and melting temperature for various types of biobased polyvinyl acetals were evaluated and compared with a commercial product polyvinyl butyral (PVB). The above mentioned properties for polyvinyl hexanal (PVH) are comparable to PVB, suggesting that biobased PVH could potentially become a marketable green polyvinyl acetal polymer.

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TABLE OF CONTENTS

LIST OF TABLES	viii
LIST OF FIGURES	x
Chapter 1: Introduction	1
1.1 Research Motivation and Rationale	1
1.2 Biobased Polymers	2
1.3 Vegetable Oil Chemistry	4
1.4 Vegetable Oil Based Polymers	6
1.5 Organization of the dissertation	10
Chapter 2: Method Implementation for Ozonolysis Product Characterization and Mass Balance Study	14
2.1 Introduction	14
2.1.1 Ozone chemistry	14
2.1.2 Ozonation of fatty acid group	16
2.1.3 Ozonolysis of soybean-oil-based FAMES	20
2.1.4 Analysis method for ozonolysis products	23
2.2 Experiment	25
2.2.1 Materials	25
2.2.2 Continuous reaction	25
2.2.3 Oxone treatment	27
2.2.4 GC analysis	28
2.2.5 GC-MS analysis	29
2.3 Results and Discussion	29
2.3.1 Composition of reactants and products	29
2.3.2 Effective carbon number method for quantitative GC-FID analysis	33
2.3.3 Ozonolysis in methanol system	37
2.3.4 Ozonolysis in water system	41
2.4 Conclusions	45
Chapter 3: Mass Transfer and Reaction Kinetics Study for Ozonation of FAMES .	47
3.1 Introduction	47
3.2 Experiment	50
3.2.1 Ozone measurement	50
3.2.2 GC analysis	52
3.2.3 Ozonolysis reaction	52
3.2.4 Ozonolysis of FAMES in methanol	52
3.2.5 Ozonolysis of FAMES in water	53
3.2.6 Mass transfer model of ozone in methanol and water	53
3.2.7 Assumptions of model and Henry's law constant measurement	58
3.2.8 Extraction of organic products from solution after Oxone treatment	59
3.3 Results and Discussion	60

3.3.1	Reaction kinetics of ozonolysis in methanol system	60
3.3.1.1	Batch process	60
3.3.1.2	Continuous process	65
3.3.2	Oxone treatment and extraction of ozonolysis products in methanol system	69
3.3.3	Mass transfer study of ozone in methanol system	73
3.3.4	Ozone mass transfer in water system.....	78
3.3.5	Ozone mass transfer under reaction in methanol system.....	79
3.3.6	Reaction kinetics of ozonolysis in water system	82
3.3.6.1	Batch process	82
3.3.6.2	Continuous process	86
3.4	Conclusion.....	89
Chapter 4: Distillation Process Design to Separate Ozonolysis Products of FAMES		92
4.1	Introduction	92
4.2	Heuristic method to determine distillation sequence	94
4.3	Distillation sequence for ozonolysis products.....	95
4.4	Properties for main components.....	98
4.5	Distillation design	101
4.6	Results and discussion.....	103
4.6.1	Distillation design for separation of products obtained from ozonolysis in methanol	103
4.6.2	Distillation design for products obtained from ozonolysis in water	108
4.7	Conclusion.....	115
Chapter 5: Simulation of Wiped Film Distillation in Aspen Plus		116
5.1	Introduction	116
5.2	Experiment	120
5.2.1	Materials.....	120
5.2.2	Analytical methods	120
5.2.3	Wiped film distillation	121
5.2.4	Simulation in Aspen Plus	123
5.3	Results and discussion.....	124
5.3.1	Affecting factors in WFD	124
5.3.2	Vapor pressure data comparison and regression.....	129
5.3.3	Simulation in Aspen for methanol and methyl hexanoate mixture	132
5.3.4	Simulation in Aspen for ozonolysis product mixture	134
5.3.5	Simulation in Aspen for FAMES mixture	137
5.4	Conclusion.....	140
Chapter 6: Polyvinyl Acetal Synthesis and Characterization		142
6.1	Introduction	142
6.2	Experiments.....	145
6.2.1	Materials.....	145
6.2.2	Preparation of PVOH solution	146
6.2.3	Preparation of polyvinyl acetal in aqueous solution	146

6.2.4	Preparation of polyvinyl hexanal in organic solution	147
6.2.5	Thermogravimetric analysis (TGA).....	147
6.2.6	Differential scanning calorimetry (DSC).....	148
6.2.7	Gel permeation chromatography (GPC) for molecular weight measurement	148
6.2.8	¹ H NMR analysis	148
6.3	Results and Discussion.....	149
6.3.1	Thermogravimetric analysis (TGA).....	149
6.3.2	Differential scanning calorimetry (DSC).....	154
6.3.3	Gel permeation chromatography (GPC) for molecular weight measurement	157
6.3.4	¹ H NMR analysis for PVH prepared in aqueous solution.....	158
6.4	Conclusion.....	159
BIBLIOGRAPHY		163

LIST OF TABLES

Table 1.1 Properties and fatty acid compositions of the most common vegetable oils	7
Table 2.1 Compositions of FAMES	31
Table 2.2 Identification of ozonolysis products formed in ethanol and water system, with respective mass spectra reliability according to NIST databank.	32
Table 2.3 Contributions to the Effective Carbon Number	34
Table 2.4 Calculated Effective Carbon Numbers for main compounds	36
Table 2.5 Comparison between experimentally obtained ECN and calculated ECN	37
Table 2.6 Yield for products from ozonolysis in methyl system	39
Table 2.7 Yield for products after Oxone treatment	41
Table 2.8 Yield for products from ozonolysis in water system	44
Table 2.9 Mass yield of products from ozonolysis in two systems	45
Table 4.1 Products generated from ozonolysis in methanol after Oxone treatment and water extraction.....	96
Table 4.2 Molar ratio of compounds after removing water and methanol	97
Table 4.3 Products generated from ozonolysis in water	98
Table 4.4 Properties for main products from ozonolysis	100
Table 4.5 Distillation results for the products from ozonolysis of FAMES in methanol	105
Table 4.6 Reboiler and condenser design specification for separating products from ozonolysis of FAMES in methanol	107
Table 4.7 Distillation column design specification for separating products from ozonolysis of FAMES in methanol	108
Table 4.8 Distillation result for products from ozonolysis in water	111
Table 4.9 Reboiler and condenser design specification for products from ozonolysis in water.....	112
Table 4.10 Distillation column design specification for products from ozonolysis in water	113

Table 4.11 Comparison of two distillation processes based on the same input of FAMEs	114
Table 5.1 Dimensions of ICL-04 wiped film evaporator.....	122
Table 5.2 Modeling and experimental data comparison of component flow rates in distillate stream.	133
Table 6.1 Average molar mass of PVH made in two different solvents	158

LIST OF FIGURES

Figure 1.1 Structure of triglyceride	5
Figure 2.1 Natural formation of O ₃	14
Figure 2.2 Ozonation mechanisms in methanol and water system	17
Figure 2.3 Ozonolysis reaction in methanol system	21
Figure 2.4 Ozonolysis reaction in water system	22
Figure 2.5 Reaction process and equipments for ozonolysis. A: air cylinder; B: ozonator; C: ozone analyzer; D: plug flow reactor; E: batch reactor; F: flow meter; G: dry ice trap; H: potassium iodide trap; c: cooling water; g: gas; m: liquid material.	26
Figure 2.6 Oxone oxidization reaction mechanisms.	27
Figure 2.7 GC chromatograph for soybean oil FAMES. 1: Methyl palmitate (C16:0); 2: Methyl Stearate (C18:0); 3: Methyl oleate (C18:1); 4: Methyl linoleate (C18:2); 5: Methyl linolenate (C18:3).	30
Figure 2.8 Chromatogram for products from ozonolysis in methanol system. A: Hexanal; B: Methyl hexanoate; C: Nonanal; D: Methyl nonanoate; E: Methyl 9-oxononanoate; F: Dimethyl azelate; G: Methyl palmitate; H: Methyl stearate.	39
Figure 2.9 Chromatogram for products after oxone treatment. A: Hexanal; B: Methyl hexanoate; C: Nonanal; D: Methyl nonanoate; E: Methyl 9-oxononanoate; F: Dimethyl azelate; G: Methyl palmitate; H: Methyl stearate.	40
Figure 2.10 Chromatogram for products of ozonolysis in water system. A: Hexanal; B: Nonanal; C: Methyl 9-oxononanoate; D: Methyl palmitate; E: Methyl stearate.	42
Figure 2.11 Chromatogram for acid products of ozonolysis in water system. A: Hexanoic acid; B: Nonanoic acid; C: Monomethyl azelate	43
Figure 3.1 GC chromatograms for FAMES in methanol solution during ozonolysis in semi-batch reactor. Oxygen/ozone gas mixture flow rate was 1 L/min, with 10 wt% of ozone. A: Methyl palmitate; B: Methyl Stearate; C: Methyl oleate; D: Methyl linoleate; E: Methyl linolenate; F: Hexanal; G: Nonanal; H: Methyl 9-oxononanoate; I: Dimethyl azelate.	61

Figure 3.2 Ozonolysis of FAMES in three cooling systems using methanol as solvent system.....	62
Figure 3.3 Molar yields of products from ozonolysis in methanol in plug flow reactor under different flow rates.	66
Figure 3.4 Total molar yields for products obtained from the same reactants from ozonolysis in methanol in plug flow reactor under different flow rates	67
Figure 3.5 Conversion of unsaturated FAMES during ozonolysis in methanol in plug flow reactor under different flow rates.....	68
Figure 3.6 Kinetics for Oxone treatment of ozonolysis products	70
Figure 3.7 GC chromatograms for products before and after Oxone treatment. A: Hexanal; B: Methyl hexanal; C: Nonanal; D: Methyl nonanoate; E: Methyl 9-oxononanoate; F: Dimethyl azelate; G: Methyl palmitate; H: Methyl stearate.	71
Figure 3.8 Extraction of products after Oxone treatment using hexane. From batch 1 to 5, the volumetric ratios of sample to extractant were 4:6, 4:4, 4:3, 4:2 and 4:1.	72
Figure 3.9 Extraction of products after Oxone treatment using water. From batch 1 to 5, the volumetric ratios of sample to extractant were 4:6, 4:4, 4:3, 4:2 and 4:1.	73
Figure 3.10 Concentration of ozone in methanol under different solvent flow rate at 22 °C with total gas pressure 20.89 psi, flow rate 3.75 L/min and ozone mass fraction 10.95%.	74
Figure 3.11 Gas phase NTU for ozone in methanol for PFR reactor under different solvent flow rate at 22 °C with total gas pressure 20.89 psi, flow rate 3.75 L/min and ozone mass fraction 10.95%.	75
Figure 3.12 Box plot of gas phase NTU for ozone mass transfer in methanol in PFR reactor under different solvent flow rate at 22 °C with total gas pressure 20.89 psi, flow rate 3.75 L/min and ozone mass fraction 10.95%.	76
Figure 3.13 Liquid phase NTU for ozone in methanol in PFR reactor under different solvent flow rate at 22 °C with total gas pressure 20.89 psi, flow rate 3.75 L/min and ozone mass fraction 10.95%.	77
Figure 3.14 Concentration of ozone in water with different solvent flow rate at 22 °C with total gas pressure 20.89 psi, flow rate 3.75 L/min and ozone mass fraction 10.95%.	79

Figure 3.15 Ozone consumption and enhancement factor for ozone mass transfer with ozonolysis in methanol in PFR reactor under different material flow rate at 22 °C with total gas pressure 21.5 psi, flow rate 3.77 L/min and ozone mass fraction 10.11%.	81
Figure 3.16 Temperature of solution during ozonolysis reaction	83
Figure 3.17 pH change of water phase during reaction	83
Figure 3.18 Ozonolysis of FAMES in two solvent systems at room temperature	85
Figure 3.19 Conversions of unsaturated FAMES at different material flow rate for ozonolysis in water in continuous reactor.	87
Figure 3.20 Product yields at different material flow rate for ozonolysis in water in continuous reactor.	88
Figure 3.21 Total molar yields for products obtained from the same reactants from ozonolysis in water in plug flow reactor under different flow rates.	89
Figure 4.1 Distillation design in Aspen Plus for separating FAME ozonolysis products in methanol system. DIS1: methanol; DIS3: methyl hexanoate; RES3: methyl nonanoate; DIS4: dimethyl azelate; RES4: methyl palmitate and methyl stearate.	104
Figure 4.2 Distillation design in Aspen Plus for products made in water using ozonolysis. D2: hexanal; R2: nonanal; D3: methyl 9-oxononanoate; R3: methyl palmitate and methyl stearate.	110
Figure 5.1 Wiped film evaporator and adjunctive facilities. A. Wiped film evaporator; A-1. Rolling speed meter; A-2. Wiper; A-3. Heating area; A-4. Dry ice trap; A-5. Pressure gage; A-6. Condenser; B. Oil heating system; C. Peristaltic Pump; D. Material container; E. Vacuum pump; F. Water cooling system.	122
Figure 5.2 Effect of heating temperature on the ratio between distillate and feed using ozonolysis product with input flow rate of 3 ml/min and wiper rolling speed of 250 rpm, under still pressure of 2.7 kPa.	125
Figure 5.3 Effect of heating temperature on mass fraction of components using ozonolysis product with input flow rate of 3 ml/min and wiper rolling speed of 250 rpm, under still pressure of 2.7 kPa. A: Methyl hexanoate; B: Methyl nonanoate; C: Dimethyl azelate; D: Methyl palmitate; E: Methyl stearate.	126

Figure 5.4 Effect of feed material flow rate on ratio of distillate to feed using ozonolysis product with wiper rolling speed of 250 rpm, heating temperature of 60 °C under pressure of 2.7 kPa.	127
Figure 5.5 Effect of wiper rolling speed on ratio of distillate to feed using ozonolysis product with feed flow rate of 3 ml/min, heating temperature of 60 °C under pressure of 2.7 kPa.....	128
Figure 5.6 Comparison of vapor pressure for methyl esters from Aspen (continuous data) and literature (discrete points). C7: methyl hexanoate; C10: methyl nonanoate; C11: dimethyl azelate; C17: methyl palmitate; C19: methyl stearate.	130
Figure 5.7 Comparison of vapor pressure data for unsaturated fatty acid methyl esters from Aspen and literature. (C18:1): methyl oleate; (C18:3): methyl linolenate.	131
Figure 5.8 Comparison of vapor pressure data of methyl linoleate from Aspen (databank and after regression) and literature.	132
Figure 5.9 Bubble pressure of mixture versus modeling pressure from Aspen.	134
Figure 5.10 Comparison of component flow rate in distillate for experimental and modeling data of saturated methyl ester mixture. METH: Methanol; C7: Methyl hexanoate; C10: Methyl nonanoate; C11: Dimethyl azelate; C17: Methyl palmitate; C19: Methyl stearate.	136
Figure 5.11 Bubble pressure of mixture versus modeling pressure in Aspen for products prepared through ozonolysis. Operating pressure was 1 atm, feed flow rate was 3 ml/min, condenser temperature was 3 °C, and the rolling speed of wiper was 250 rpm.	137
Figure 5.12 Experimental and modeling data comparison of component flow rate in distillate for separation of FAMES. C17:0: Methyl palmitate; C19:0: Methyl stearate; C18:1: Methyl oleate; C18:2: Methyl linoleate; C18:3: Methyl linolenate.	139
Figure 5.13 Experimental pressure of WFD versus modeling pressure in Aspen for FAMES. Operating temperature was 170 °C, feed flow rate was 3 ml/min, condenser temperature was 3 °C, and the rolling speed of wiper was 250 rpm.	140
Figure 6.1 Reactions for polyvinyl acetal polymer preparation.	143
Figure 6.2 TGA weight percentage change with temperature profiles of polyvinyl alcohol and acetal polymers.	150

Figure 6.3 TGA weight percentage change with temperature profiles of polyvinyl alcohol and acetal polymers.....	152
Figure 6.4 DSC spectra of polyvinyl acetals. PVB: polyvinyl butyral provided by Kuraray; PVOH: polyvinyl alcohol provided by Kuraray; PVH: polyvinyl alcohol reacted with hexanal based on stoichiometry; PVH_2: polyvinyl alcohol reacted with 100% excess hexanal based on stoichiometry; PVH_1/2: polyvinyl alcohol reacted with half amount of hexanal based on stoichiometry.	155
Figure 6.5 DSC spectra of polyvinyl acetals. PVB: polyvinyl butyral provided by Kuraray; PVH: polyvinyl alcohol reacted with hexanal based on stoichiometry; PVN: polyvinyl alcohol reacted with nonanal based on stoichiometry; PVHN: polyvinyl alcohol reacted with hexanal and nonanal (molar ratio 1:1) based on stoichiometry; PVHN9: polyvinyl alcohol reacted with hexanal and 9-oxononanoate (molar ratio 1:1) based on stoichiometry.....	156
Figure 6.6 GPC spectrum of PVH made in two different solvents.....	158
Figure 6.7 ¹ H NMR spectrum of PVH prepared in organic solvent	159

Chapter 1: Introduction

1.1 Research Motivation and Rationale

A polymer is a large molecule containing repeated subunits which is usually produced from monomers. Polymers are widely used in many areas including textiles, packaging, medicines, construction, etc. In 2013, the world's plastic production was more than 299 billion kilograms [1], and it is predicted that the global production will surpass 300 million tons by 2015. Currently, most commercially available polymers are derived from non-renewable resources and account for approximately 7% of the overall worldwide oil and gas usage [2]. Since the early 20th century, petroleum has been the main resource for world's energy and chemical production, including polymer precursors. To satisfy energy and chemicals demand, the world currently consumes about $14.26 \times 10^6 \text{ m}^3$ of petroleum per day (by May 30, 2013, from US Energy Information Administration [3]) and about 16% of this volume is consumed by the chemical industry. Due to intense consumption of fossil energy, the conventional crude oil production has already reached a peak and is depleting at a rate of 6.8% annually, according to the report from the International Energy Agency's (IEA) 2010 World Energy Outlook [4]. On the other hand, fossil energy consumption also has a strong impact on the environmental conservation. As is well known, fossil carbons have been immobilized underground for millions of years and once being released for energy or chemical production, more carbons will be exposed to the surface of the planet. As a significant portion of the carbons are fully oxidized during combustion of fossil fuel, they are released in the form of carbon dioxide, which is a key factor responsible for the greenhouse effect and global warming. To alleviate or solve the

problem, the usage of renewable carbon for fuels and chemicals production is required. In response to these environmental concerns, biobased polymers have been developed.

Biobased polymers, as renewable substitutes to traditional petroleum-based plastics, can be derived from a wide range of feedstocks such as corn, soybeans, wood and crop stalks [5]. Among the biobased polymer resources, soybean is the one of the best choices in terms of availability and cost. US is the largest soybean producer in the world, producing more than 100 million tons of soybeans in 2014 [6] and exporting about one third of the production. Aiming to reduce the consumption of fossil resources and to explore the industrial utilization of soybean, an environmentally friendly process for production of polymer precursors and other value-added products from soybean oil was studied in this work. Furthermore, the synthesis and characterization of a novel soybean oil based polymer is presented in this study.

1.2 Biobased Polymers

Biobased polymers are polymers derived from renewable biomass resources, such as vegetable fats and oils, corn or pea starch, wood, etc. Some biobased polymers are designed to be biodegradable, but a biobased polymer is not necessarily biodegradable. Biodegradable polymers such as polylactic acid, starch plastics and polyhydroxyalkanoates, are defined as materials whose physical and chemical properties undergo deterioration and completely degrade to form carbon dioxide, methane, and water when exposed to microorganisms. Biobased polymers can be classified into renewable resource based polymers and mixed sources (bio-/petro-) based polymers, depending on the proportion of bioresource [7].

Biobased polymers still take a very small portion in the total global plastic market (less than 1%) and it is expected that biobased polymers will account for just over 1% by 2015 [8]. However, as the bioeconomy develops and people become more environmentally conscious, there will be an increasing demand for developing sustainable polymers, derived from biomass, which can replace petroleum based polymers in various applications.

The resources for biobased polymers were mainly from food products in the early technological stages, and included potatoes, corn grain and any other starch-producing crop. However, the usage of food products for polymer production and other commodities raises ethical problems due to increase in food demand and price. Therefore, the focus has been shifted to use non-edible biomass and organic waste for production of biobased materials [9].

Since polymers are usually synthesized through the reaction of monomers, the development of biobased polymers often starts from production of small molecules which will constitute the macromolecule. There are three main methods to get the small molecules for polymer building blocks from natural resources — extraction, fermentation and chemical synthesis [10]. Biobased polymers that have the monomers derived from the first method include starch, cellulose and lignin. The fermentation method is used to produce polymers like some types of polyhydroxyalkanoates, while traditional chemical synthesis method is more suitable for manufacturing some widely used polymers like polylactic acid (PLA), polyethylene (PE), etc [10].

Biobased polymers are widely applied in many industrial areas such as food packaging, medical material, clothing textiles, coating, etc. The reason for this is that most biobased polymers share some properties with traditional petroleum-based polymers and, at the same time, they have some distinctive characteristics. For example, PLA – one of the most famous biobased polymers – is widely used in packaging because it is very similar to polyethylene terephthalate (PET), except for a lower degradation temperature (60 °C). Unlike PET, PLA is also biodegradable [11] and therefore, it can be used in medical materials like sutures, which need to degrade in a special condition after some time [12].

The main challenges for wider commercialization of biobased polymers are the performance of these polymers and the manufacturing cost. The former challenge may be reduced if fossil-based polymers can be slowly replaced by biobased polymers that have been proved to meet performance parameters for certain applications, while at the same time, new biobased polymers with superior properties for new applications can be developed. The latter challenge will be reduced as fossil energy is depleted and the demand for biobased polymer development increases.

1.3 Vegetable Oil Chemistry

Vegetable Oil is usually produced from plant components (typically from seeds), and two different methods are mainly used to extract vegetable oil: 1) mechanical extraction with a mill and 2) chemical extraction with a solvent [13]. The most popular mechanical extraction method is expeller pressing, which is operated at high pressure to obtain the maximum yield. This method can also be specified as cold pressing if it is operated at temperatures lower than 120 °C, otherwise it is designated as regular expeller pressing. Besides the above two methods, there is also CO₂ extraction, in which carbon dioxide is

converted to liquid, making it a safe and effective solvent that allows all the desirable active constituents of a plant to be collected without the risk of heat degradation [14]. Mechanical extraction is preferred in food industry, since it will not introduce other chemicals into the product, while the chemical solvent extraction (e.g. hexane) is more preferred in chemical industry, which uses vegetable oil as feedstock for the manufacture of chemicals [13].

As shown in Figure 1.1, the main components of vegetable oil are triglycerides, which is a group of compounds with a structure of three fatty acids linked to one glycerol molecule. The length of carbon chain of those fatty acids as well as the number of double-carbon bonds determines the physical and chemical properties of vegetable oil. The number of carbons in saturated fatty acids varies from 8 to 24 and in unsaturated fatty acids it varies from 16 to 24, while the number of double bonds in the main chain of unsaturated fatty acids ranges from 1 to 3 [15]. Vegetable oil has a lower boiling point than fat because it contains a higher percentage of unsaturated fatty acids. This structural feature is an important advantage of vegetable oil over animal fat for its application in the chemical and polymer industry. Vegetable oils have been used for manufacturing paints and coatings for centuries and during the last decade, a variety of vegetable oil-based fuels has been increasingly produced [16].

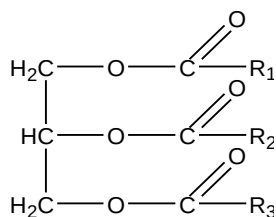


Figure 1.1 Structure of triglyceride

The chemical structure of triglycerides contains two reactive sites, which are the double bonds in the unsaturated fatty acid chains and the ester groups that connect all the fatty acid chains to the glycerol structure [17]. Most vegetable oil-based polymers were synthesized using chemistry targeting those two reactive sites. For example, biorenewable polymers can be prepared by hydrogenation, epoxidation, carboxylation, oxidative cleavage or polymerization, taking advantage of the carbon-carbon double bonds in the fatty acid chains [18]. Reactions targeting the ester linkages encompass hydrolysis, transesterification, amide synthesis, etc [19]. Innovative design and synthesis of new vegetable oil-based monomers and the incorporation of novel polymerization methods will impel the development of novel vegetable oil derived polymeric materials in the future.

1.4 Vegetable Oil Based Polymers

Based on the triglyceride structure, a great variety of vegetable-oil-based polymers have been derived from reactions targeting double bonds, allylic positions and the ester groups. There are many types of plants that can be used to produce vegetable oil. The main difference among vegetable oils is determined by the fatty acids contained in the triglyceride molecules. Different fatty acids have different length of carbon chain and different number of double bonds. The carbon number of most fatty acids falls into the range of 8 to 18 [2]. The five main fatty acids can make up to 94 wt% ~ 100wt% of the commonly used vegetable oils (Table 1.1 [2]). For polymer synthesis depending on double bond-related reactions, the presence of more double bonds will certainly lead to higher yield of polymeric products. In Table 1.1, it is shown that soybean oil has higher double bond ratio than most of the other listed vegetable oils. This fact supports the

choice of soybean oil as the starting material used in this project, besides the wide availability and low price.

Table 1.1 Properties and fatty acid compositions of the most common vegetable oils

Vegetable oil	Double bonds ^a	Iodine value ^b /mg per 100 g	Fatty acids (%)				
			Palmitic	Stearic	Oleic	Linoleic	Linolenic
Palm	1.7	44–58	42.8	4.2	40.5	10.1	—
Olive	2.8	75–94	13.7	2.5	71.1	10	0.6
Groundnut	3.4	80–106	11.4	2.4	48.3	31.9	—
Rapeseed	3.8	94–120	4	2	56	26	10
Sesame	3.9	103–116	9	6	41	43	1
Cottonseed	3.9	90–119	21.6	2.6	18.6	54.4	0.7
Corn	4.5	102–130	10.9	2	25.4	59.6	1.2
Soybean	4.6	117–143	11	4	23.4	53.3	7.8
Sunflower	4.7	110–143	5.2	2.7	37.2	53.8	1
Linseed	6.6	168–204	5.5	3.5	19.1	15.3	56.6

^aAverage number of double bonds per triglyceride.

^bThe amount of iodine (mg) that reacts with the double bonds in 100 g of vegetable oil.

Polyurethane is one of most important polymeric materials that can be synthesized by triglycerides. Polyurethanes are usually synthesized from reaction of polyols with multi-isocyanate, and both reactants could be derived from triglycerides and their derivatives [20]. Soybean oil triglycerides were used to synthesize soybean oil iodo isocyanate through a reaction between double bonds from the fatty acids and iodine isocyanate [21]. Fatty acids, e.g. oleic acid could also be used to produce multi-isocyanates [22, 23], and it was found that diesters were applied as the starting material for diisocyanate synthesis. Vegetable oil based polyols could be synthesized through many methods including thiol-ene coupling reactions [24-26], ozonolysis [27, 28], epoxidation, ring-opening [29], etc. The starting materials that have been reported include castor oil [30], sunflower oil, canola oil, soybean oil and linseed oil .

Polyesters are another type of polymers that can be produced from vegetable oil. Biobased polyesters could be synthesized through condensation polymerization of monoglycerides with phthalic anhydride [31]. It was also found that polyesters could be obtained by reacting epoxidized oils with dicarboxylic acid anhydrides with tertiary amines or imidazoles as catalyst [32]. The properties of polyesters are usually determined by the structure of dicarboxylic anhydride, the dicarboxylic anhydride and epoxy reactant ratio [31].

Due to the special structure of some free acids in vegetable oil, polyesters can be synthesized directly from these fatty acids. For example, ricinoleic acid represents more than 90% of castor oil composition, it contains both carboxyl and hydroxyl groups and therefore provides the structural condition for self-polymerization and formation of polyester [33]. Another important fatty acid is sebacic acid, which has also been used to synthesize polyester [34]. This product has potential in biomedical applications due to its shape-memory property.

By applying ozonolysis, part of the unsaturated fatty acids can be converted into diacids since ozone can oxidize the double bonds into carboxylic groups [35]. Published work includes ozonolysis on oleic acid, petroselinic acid and erucic acid [35]. Considering the safety issue of ozone usage, a process using peracetic acid and ruthenium catalysts or H_2O_2 and Mo, W, or Re based catalysts has been proposed as an alternative oxidation method, however, they only allowed diacid molar yields between 50 and 60% [35].

Epoxidized vegetable oils as starting materials will lead to the syntheses of another type of vegetable-oil-based polymer, notably an epoxy resin. Epoxidation of soybean oil was carried out in toluene with the presence of an ion exchange resin as the catalyst. It was

found that the reaction was first-order with respect to the double bond concentration and very little amount of side products were produced during the reaction [36]. Epoxidized vegetable oils including castor, soybean and linseed oils can be polymerized with utilization of photo-initiators [37]. The research on catalytic epoxidation of methyl linoleate, using methyltrioxorhenium and pyridine as catalysts in aqueous H_2O_2 was also reported, and it was observed that the epoxidation reaction completed within 4 hours [38]. Ring-opening polymerization of epoxidized methyl oleate was studied with ionic-coordinative initiators present, and the molecular weight of the polymer could reach to over 7000 g/mol [39].

Polyolefin with its known high chemical stability and biocompatibility has also been considered as one of biobased polymers derived from vegetable oil. Similar to epoxy resin, the target reactive group for polymerization is also the double bond. One method to synthesize polyolefin is cationical polymerization in a supercritical dioxide medium with the presence of boron trifluoride diethyl etherate [40], and products produced in this process can be used as medical lubricants. Another approach that has been developed was acyclic diene metathesis (ADMET) polymerization of double bonds in soybean oil by using Grubbs' ruthenium catalyst, which gave a variety of polymeric materials ranging from sticky oils to rubbers [41]. Moreover, norbornene-functionalized castor oil or linseed oil could also be used to form thermosets by employing the unique ring-opening metathesis polymerization (ROMP) pathway [42].

In this project, two types of soybean-oil-based polymers will be studied. Part of the study is about the production of diester (dimethyl azelate) through ozonolysis, which can be used as the starting material for polyesters. Another part of this project deals with the

manufacture of polyvinyl acetal polymer. Although much work has been done in the four main types of soybean-oil-based polymers, this polymer does not belong to any of the types mentioned above. The product will be formed through the reaction between aldehydes (e.g. hexanal, nonanal and 9-oxo-nonanoate) generated from ozonolysis of soybean FAMES and polyvinyl alcohol in an aqueous system in the presence of sulfuric acid. Although the polyvinyl alcohol used in the lab was petroleum based, it can also be made from biobased resources as shown in previous research [43], which implies that this polyvinyl acetal polymer can be made fully biobased.

1.5 Organization of the dissertation

This dissertation consists of 6 chapters. It starts with a general introduction about the motivation of the project and some basic knowledge related to the subject of the study. Moreover, the conclusion of the entire work and final considerations for future advancements in this line of work will be addressed.

Chapter 1 discusses the research motivation and provides a thorough review about biobased polymers, soybean oil reactions and soybean oil based polymers. It summarizes the important studies related to biobased polymers using vegetable oil as raw material. Four main types of polymers including polyurethane, polyester, epoxy resin and polyolefin are discussed respectively.

Chapter 2 describes the experiments for ozonolysis reaction in both methanol and water systems through continuous process. In the methanol system, ozonolysis was conducted with soybean oil based FAMES with the presence of sodium methoxide as catalyst, and the consequential products were oxidized further by Oxone to convert aldehydes to

esters. In the water system, soybean oil based FAMES were ozonated without using any catalyst. The composition, properties and yield of products generated from the two reaction systems were examined. Analysis methods of both GC-MS and GC-FID were used for qualitative and quantitative measurement of ozonolysis products. Since pure compound samples are not available for all the compounds, in order to calculate the concentration of some commercially unavailable compounds through GC chromatogram, the Effective Carbon Number (ECN) method was applied to estimate the response factor.

Chapter 3 covers mass transfer and reaction kinetics for ozonolysis reactions. The Number of Transfer Units (NTU) approach was used to measure the mass transfer of ozone in methanol reaction system. Reaction kinetics was investigated in both batch and continuous processes for the two solvent (methanol and water) systems. In the batch process in methanol, the impact of temperature on reaction rate was compared for three cooling conditions – water bath, ice/water bath and dry ice/acetone bath. In continuous reaction, the product yields under different flow rates for FAMES and methanol mixtures were calculated and compared. Oxone treatment was applied to convert aldehydes to methyl esters and a study on reaction rate between all-in-one load and multiple load processes were conducted. In order to purify organic products, extraction was conducted using water and hexane, and the results were compared between the two solvent systems. For ozonolysis of FAMES in the water system, temperature and pH change were investigated in a batch process and the effect of flow rate of FAMES and water mixture on product composition and yield was studied in the continuous process.

Chapter 4 focuses on distillation simulation and design of ozonolysis products using Aspen Plus. It elaborates the details of distillation column design based on consideration

of safety, product quality and energy and cost efficiency. Distillation sequence for all the compounds was firstly determined by a heuristic method. Based on this distillation order, specific column design was conducted for products generated using ozonolysis in both water and methanol system. The operation temperature, pressure, column dimensions, number of stages and input stages were all specified and optimized.

Chapter 5 demonstrates a model for predicting the separation profile of the ozonolysis products from soybean oil derived FAMES using wiped film distillation. Wiped film distillation unlike fractional distillation cannot be simulated directly using existing software. This means that given certain operation conditions, the separation results (e.g. distillate rate and composition) cannot be easily calculated or estimated. On the other hand, given target product purity, separation conditions can be determined by an empirical method. In this chapter, wiped film distillation is modeled in Aspen Plus by fitting an objective function. A correlation between the pseudo vapor pressure calculated from the operating temperature in the wiped film separator and pressure in Aspen Flash module is then examined.

Chapter 6 exhibits the syntheses of polyvinyl acetal polymers using aldehydes produced through ozonolysis. The three aldehydes, hexanal, nonanal and 9-oxo-nonanoate as the main products prepared through ozonolysis of FAMES in water system, react with polyvinyl alcohol, and form a series of polyvinyl acetal polymers. The thermal properties of these polymers were analyzed using TGA and DSC, the molecular weight was calculated based on the data from GPC and the extent of reaction and polymer structure was determined by ^1NMR . These characteristics were also compared to a well known

similar product in the market, polyvinyl butyral (PVB), to evaluate potential industrial applications.

Chapter 2: Method Implementation for Ozonolysis Product Characterization and Mass Balance Study

2.1 Introduction

2.1.1 Ozone chemistry

Ozone was first identified as a distinct chemical compound by Christian Friedrich Schönbein in 1828 [44] and the molecular formula was determined by Soret in 1865 [44]. Ozone (or trioxygen) is an inorganic compound that contains three atoms of oxygen with the chemical formula O_3 . According to experimental evidence from microwave spectroscopy, ozone is a bent molecule, with C_{2v} symmetry. The O - O distance is 127.2 pm (1.272 Å) and the O - O - O angle is 116.78° [45]. In high concentration ozone is a bluish green gas. It has a very strong pungent smell which is noticeable even at very low level ($0.01 \mu\text{mol/mol}$) in air [46]. Exposure in more than $0.1 \mu\text{mol/mol}$ of ozone may cause headache, burning eyes and irritation to the respiratory passages [47].

The formation of ozone in the stratosphere is a natural photodissociation process (Figure 2.1) in which ultraviolet solar radiation breaks down the chemical bonds of atmospheric O_2 molecules, and the free radical oxygen atoms combine with O_2 to form ozone.

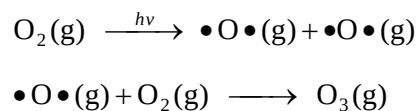


Figure 2.1 Natural formation of O_3

Traditional ways of producing ozone include 1) corona discharge and 2) ultraviolet light methods [48, 49]. New generators may use 1) cold plasma or 2) electrolytic method [50].

The former method applies pure oxygen as the input source and this input gas is exposed to plasma created by a dielectric barrier discharge. The molecular oxygen is therefore split into single atoms and these free atoms recombine in triplets to form ozone. The maximum concentration of ozone produced with this method is about 5%. The electrolytic method can achieve a higher purity of 20 to 30% by using water as the source of ozone production. Current ozone generators differentiate from each other by the design of the electrodes. For a required production above 20 kg/hour, a gas/water tube heat-exchanger will be installed, as ground electrode and tubular high-voltage electrodes will be assembled on the gas-side [51].

Ozone is not as stable as oxygen, and it tends to decay into diatomic oxygen in a very short time. This reaction proceeds more rapidly with increased temperature and increased pressure, so ozone cannot be stored or transported and must be produced on site. Since ozone is a powerful oxidizing agent, only a few materials can be used for handling or storage, like stainless steel, titanium, aluminium, glass, polyvinylidene fluoride, etc.

Ozone has a very high oxidizability and reacts with many different types of compounds, such as metals, nitrogen and carbon compounds, sulfur compounds, alkenes, alkynes, etc. Because of this, ozone has a wide application in many areas in industry. For example, ozone is used as disinfectant in hospitals and food factories; ozone can also be used as deodorizer for air and objects and sanitizer for swimming pools and spas; ozone is added in dish washers to kill yeast, mold and bacteria; ozone is introduced to age rubber samples and determine the useful life of a batch of rubber; ozone is also applied in manufacture of chemical products [52].

2.1.2 Ozonation of fatty acid group

Biobased polymers have drawn attention of researchers because biobased resources are widely available, renewable, environmentally friendly and relatively safe to human [53]. Among all the studies, the research on fatty acids derived from vegetable oil is one of the major topics researched. A considerable amount of research related to the chemical modification and polymerization of fatty acids on unsaturated bonds has been reported. Generally, two main strategies can be adopted to convert fatty acids into monomers: creating new reactive functional groups based on original structure; splitting the fatty acid chains at the double bonds and generating new molecules. Ozonolysis is applied to follow the second strategy.

In organic chemistry, ozonation is mainly applied to react with molecules containing double or triple carbon bonds. During reaction, the carbon chain with unsaturated carbon bonds will be cleaved by ozone and converted to aldehydes, ketones or peroxidic derivatives of aldehydes and carboxylic acids. The type and composition of products are usually determined by the reactant as well as the reaction conditions such as the solvent, concentration of ozone, workup method or reagent, pH, etc.

The reaction of ozone with unsaturated carbon bonds in organic compounds was first studied in 1905 [54], following which a 3-step mechanism (Figure 2.2) was proposed by R. Criegee [55] to explain the ozonolysis reaction of alkenes. According to this mechanism, ozone reacts with double bond and forms a five-membered-ring compound called molozonide (primary ozonide). This intermediate compound decomposes to a “carbonyl oxide” group and a carbonyl compound. The decomposed products are not

stable in the system and tend to combine with each other to generate a more stable compound, similar to the primary ozonide, named ozonide (or secondary ozonide). If this reaction occurs in methanol with alkaline catalyst, the “carbonyl oxide” group will react with methanol and produce methyl esters. If this reaction happens in water, the “carbonyl oxide” group will form acids and aldehydes (or ketones), and the dominant products will be aldehyde (or ketones).

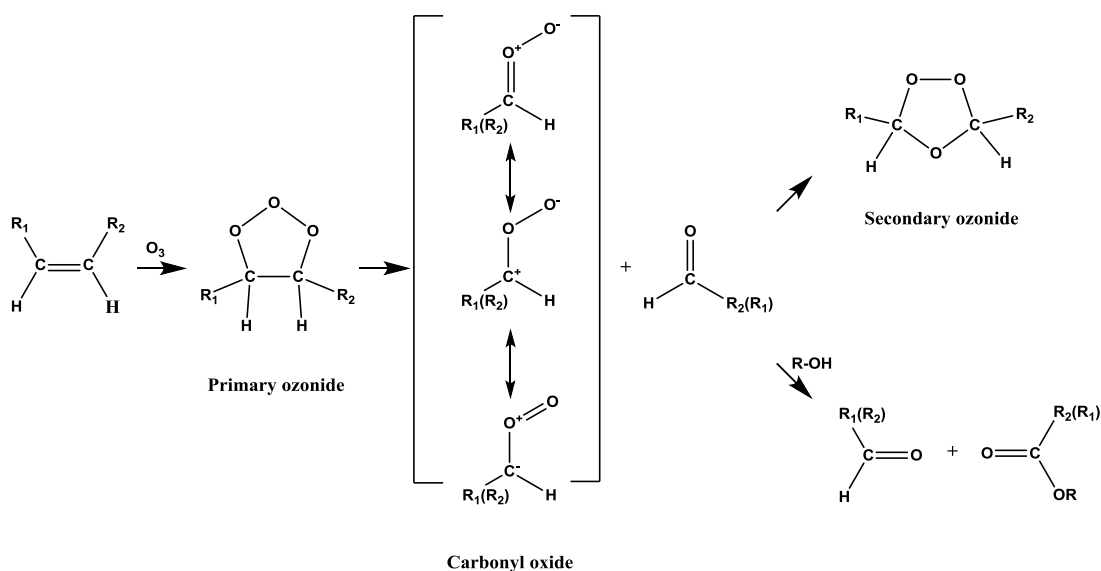


Figure 2.2 Ozonation mechanisms in methanol and water system

Due to the instability of primary ozonide generated in the intermediate step of the reaction, ozonation is usually conducted at low temperature (typically around -78 °C [55]) to prevent the ozonide from decomposing before the workup process is applied. However, in this project, the workup process was actually omitted, so the low temperature condition was not applied in the experiment.

When ozone is applied to react with double bonds, many factors including temperature, solvent and pH value should be well controlled to obtain the ideal products. Among all the factors, solvent choice can affect the reaction the most. Ozone is a strong oxidant, and the ozonation reaction usually produces a series of products, e.g. carboxylic acids, ketones, aldehydes, alcohols, etc. As shown in Figure 2.2, ozone reacts with alkene via cycloaddition and forms a primary molozonide which decomposes immediately into aldehyde and carbonyl oxides. In an aprotic solvent, the products formed from decomposition tend to react with each other to generate a more stable form of ozonide. If ozonolysis is carried out in the presence of protic solvents such as alcohols, the outcome products will consist of alkoxy hydroperoxides and/or peroxy hemi-acetals [56]. In conclusion, solvent will affect the output of ozonolysis in two aspects: it affects the amount of ozone available for the reaction (because of mass transfer efficiency), and also exerts an influence on the yield and types of products due to side reactions.

The effect of several solvents such as halogenated hydrocarbons, n-pentane, acetic acid, ethyl acetate, methanol, ethanol, and water used in ozonation has been studied by Greenwood et al. [57]. The experiment was carried out under temperature from -42 to 25 °C in different solvents, and the reaction time lasted from 5 mins to 2 hours. Based on the standpoint about resistance to attack from ozone, the conclusion from this study was that water, acetic acid, ethyl chloride, carbon tetrachloride, and monofluorotrichloromethane were satisfactory solvents for ozonation. In a practical situation, the choice of solvent should depend on the solubility of the material and the type of workup method applied. Research on the kinetics of ozonolysis of canola oil in three different solvent systems (ethyl acetate, alcohol and the mixture) under temperature from 0 to 4 °C was conducted

by Omonov et al. [56], with hexanal and nonanal as target compounds. The result showed that the better solvent was the mixture of both aprotic (ethyl acetate) and protic (methanol or ethanol) solvents which guaranteed the full solubility of canola oil and the reactivity of ozonide intermediates, thus provided a higher yield of products.

Besides the solvent, another factor that also plays an important role in ozonation is the starting material. Some researcher chose vegetable oil as the raw material like Omonov et al. [56] as described above. De Souza et al. [58] used corn oil to synthesize polyols by applying epoxidation and ozonolysis and found that epoxidation led to the opening of double bonds, while ozonolysis promoted the cleavage of double bonds and therefore reduced the molar mass of the product. The experiment was conducted in ice bath and the yield of product could reach to as high as 86%. Research on manufacture of 9-hydroxynonanoic acid methyl ester via ozonolysis from soybean oil and castor oil has also been published [59], and this compound could be used for polymer syntheses as a potential industrial application. Some other publications have focused on the ozonolysis of FAMES (fatty acid methyl esters) instead of vegetable oil. For example, it was found that by treating polyunsaturated fatty esters with ozone malonaldehyde acetals could be obtained [60]. Moreover, unsaturated FAMES were also used to produce alcohols [61]. Ozonolysis reactions on a single unsaturated FAME compound like methyl oleate were also studied and the structure of the products were analyzed [62].

Substantial studies have been presented on ozonolysis of fatty acids and fatty acid esters, however, no reference was found focusing on ozonation of three unsaturated fatty esters derived from soybean oil as a mixture, either in methanol or in water system. In addition,

ozonolysis conducted in continuous process, which will be evaluated in this project, was not mentioned in any previous work either.

2.1.3 Ozonolysis of soybean-oil-based FAMES

The starting material used in this project is FAMES derived from soybean oil, which mainly consists of five methyl esters, which are methyl palmitate, methyl stearate, methyl oleate, methyl linoleate and methyl linolenate. The former two esters are saturated and the later three esters contain 1, 2, and 3 double bonds, respectively. The total amount of the five esters takes up 97 wt% of the FAMES, where 14 wt% are saturated and 83wt% are unsaturated esters. During ozonolysis, only the three unsaturated esters participate in the reaction and the saturated ester like methyl palmitate and methyl stearate remain intact.

The composition of FAMES is determined by the source of vegetable oil and even if the FAMES are made from the same type of oil, products from different batches can be different. To keep the composition of reactant consistent, all the soybean-oil-based FAMES used in this project were acquired from the same container.

The efficiency of ozonation on FAMES highly depends on solvent, therefore choosing a proper solvent is the most critical step before starting the project. Some factors were considered while choosing the solvent, for example, the target products, the difficulty of separating the product and recycling the solvent, the cost of the solvent and the safety of the reaction. Based on all the considerations, methanol and water were selected for the following reasons: firstly, in these two solvents, the reaction initiates easily and proceeds fast even at room temperature, which implies the cost for the cooling system will

relatively low; secondly, the two solvents are cheaper than most other solvents; thirdly, methanol is volatile and therefore, solvent recycling will not be too difficult; fourthly, the compositions of output products are not very complicated, which means not many byproducts are generated, and this gives advantage to analysis and separation of products; and lastly, water is not flammable and therefore is relatively safe to operate.

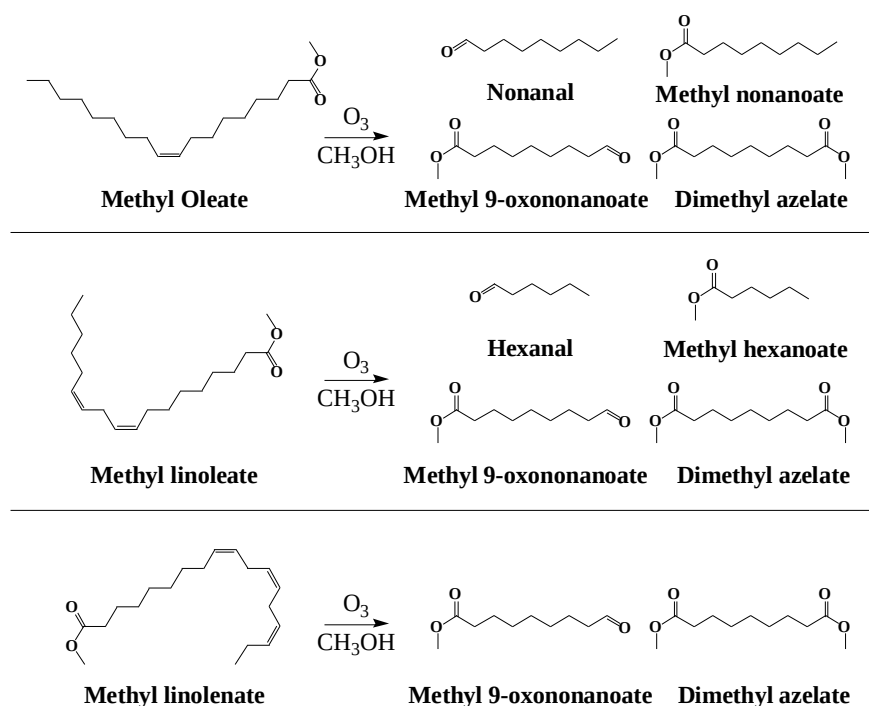


Figure 2.3 Ozonolysis reaction in methanol system

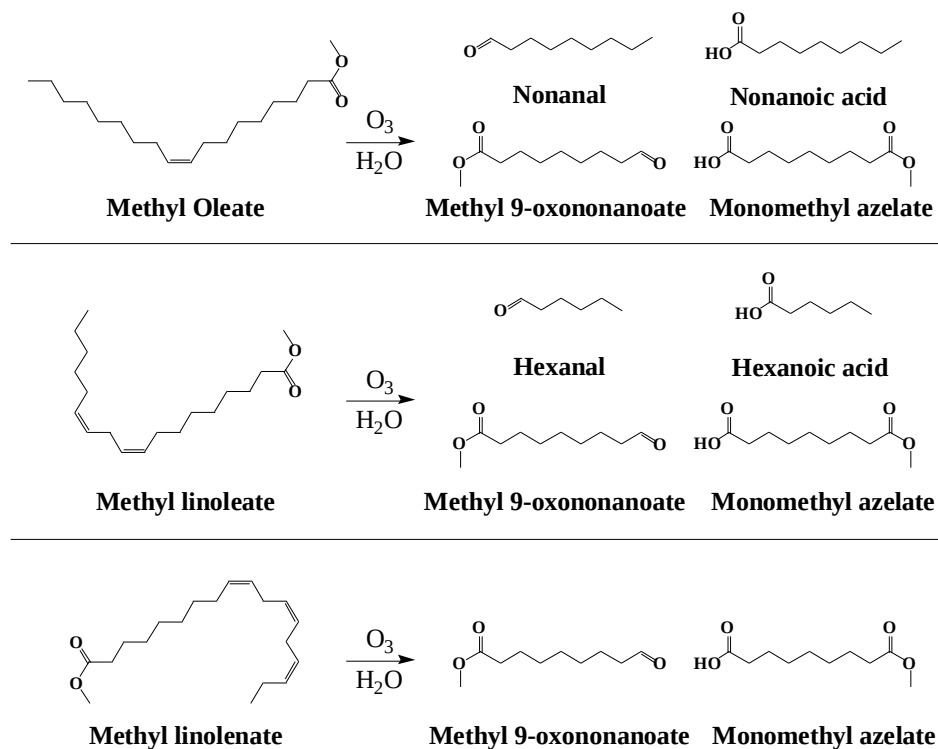


Figure 2.4 Ozonolysis reaction in water system

Ozone reacts with organic compounds by breaking down double bonds and generates formyl or carboxyl groups. The ratio of the two types of products depends on the specific reaction conditions. In methanol system, the products contain aldehydes and esters, which is because the formed carboxyl groups will react with methanol immediately and generate methyl esters. The main products are aldehydes. As shown in Figure 2.3, from the three unsaturated esters, three aldehydes are produced. Ozonolysis of methyl oleate yields nonanal and methyl nonanoate, while methyl linoleate yields hexanal and methyl hexanoate. Since half of the structure is the same for all the three esters, after being split, they share the same two products – methyl 9-oxononanoate and dimethyl ester. The ozonolysis reaction products in water, as shown in Figure 2.4 are very similar to that in methanol. The differences are that acids are formed instead esters and the yields of

aldehydes are much higher; also, no catalyst is used in water system while sodium methoxide is added as catalyst in methanol system.

2.1.4 Analysis method for ozonolysis products

The main subject of this chapter is to analyze the products prepared from ozonolysis in two solvents conducted in continuous process. The products will be firstly identified using gas chromatography-mass spectroscopy (GC-MS) before quantitative analysis is performed using gas chromatography, due to the complexity of ozonolysis products and the uncertainty of the ozonation mechanism.

Gas chromatography with flame ionization detection (GC-FID) is a well known characterization method for volatile (possessing an appreciable volatility below 350-400 °C) organic compounds. In gas chromatography, the separation unit is a glass, metal or quartz column which contains the stationary phase and mobile phase. The stationary phase is a microscopic layer of polymer on an inert solid support, and the mobile phase is a carrier gas such as helium or nitrogen. The gaseous sample molecules enter into column in mobile phase and interact with the stationary phase. Because the interaction behavior for different compounds is different, each compound will elute at a different time, known as the retention time. Comparison of retention times enables GC to do analytical work.

The technique of GC-MS as implied by the name is a combination for both GC and MS analytical methods which is usually used to analyze unknown mixtures of chemicals. The molecules are passed through and separated by the column by coming out at different retention times, after this the mass spectrometer breaks each molecule into ionized fragments and detects the fragments using the mass-to-charge ratio.

Since all the compounds in FAMES and final products are relatively volatile, GC-FID can be used as primary analysis tool. In GC-FID analysis, the concentration of a compound in solution is linearly correlated with the area of the corresponding peak in chromatogram. This correlation function, also known as calibration curve, is prepared by plotting data of peak area against compound concentration from standard samples (ideally made from pure compounds). The calculated slope of the line for each compound is the response factor, and for different compounds, the value of the factor is usually different. Once the response factor is known, the concentration can be calculated by dividing the peak area obtained from GC chromatogram by the response factor.

There is a limitation of GC analysis using the calibration curve method, because if the standard samples for certain compounds are not available, the calibration curve cannot be generated, and thus the concentration cannot be calculated. However, according to Sternberg et al. [63], the response factor for GC-FID can be examined using the effective carbon number (ECN) approach, which does not require standard samples for all compounds in the mixture. In this project, we will use this method to quantify the components for which the standard samples are not obtainable.

Another limitation for GC-FID is that samples in aqueous solution cannot be properly analyzed by it. In fact, water should be avoided from samples, because water interacts with stationary phase and may cause problems like high baseline noise or column bleed. These problems reduce the analysis sensitivity and may decrease lifetime of the column. To prevent these problems from happening, samples containing water should be extracted or dried before being injected in the GC.

2.2 Experiment

2.2.1 Materials

Soybean oil FAMES were bought from Zeeland Farm Services; methanol (99.9%), hexane (99.9%), standards for GC analysis including hexanal (99%), nonanal (98%), methyl hexanoate (99%), methyl nonanoate (98), dimethyl azelate (80%), methyl palmitate (99%), methyl stearate (99%), methyl oleate (99%), methyl linoleate (99%) and methyl linolenate (99%) were all purchased from Sigma-Aldrich (St. Louis, MO).

2.2.2 Continuous reaction

Ozone was generated by a CFS-3A ozone generator from Ozonia North America LLC. Oxygen and Ozone gas mixture flow rate was 3 L/min, with weight fraction of ozone 10%. A plug flow reactor made of steel and sealed in a PVC jacket was used. The space between the jacket and the external wall of reactor was occupied with cooling water to guarantee safety during exothermic reactions between ozone and FAMES. Both gas and liquid feeds passed injected into the reactor through two separated lines. The bottom of the reactor was equipped with a sparger to supply the ozone/oxygen gas bubbles and the internal pathway of the reactor was packed with static mixers to increase gas-liquid mass transfer during reaction. The total height of the reactor was 131 cm, the external diameter of the jacket was 12.6 cm and the internal diameter of the reactor 2.7 cm. The ozone/oxygen gas and the FAMES solution were fed into the column via separated feed lines passing through the cooling jacket to maintain a lower temperature, and then into the reactor from the bottom inlet concurrently.

Before entering the reactor, the gas feed was first passed through a Mini-Hicon ozone analyzer by which weight fraction (usually 9-13%), pressure (15-24 psi), and gas temperature (36-38 °C) were monitored. The flow rate (L/min) was measured by a flow meter (model: FM-11-10) designed by Ozone Solutions Inc.

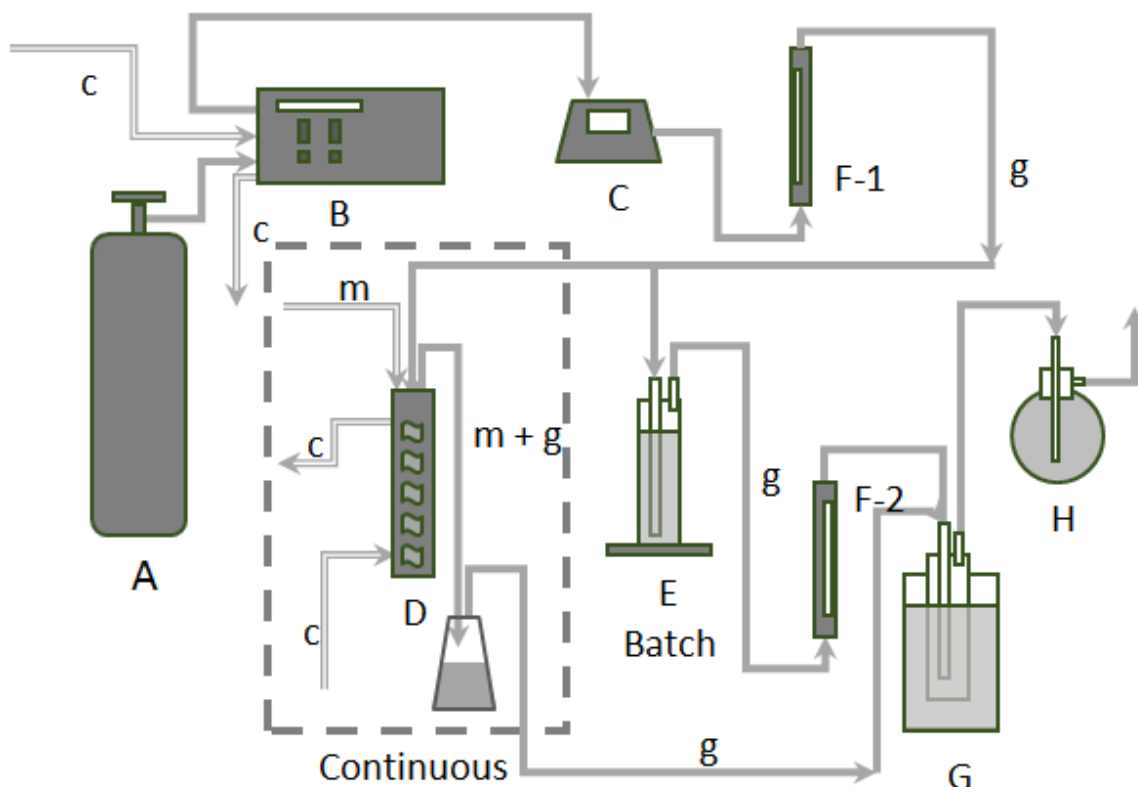


Figure 2.5 Reaction process and equipments for ozonolysis. A: air cylinder; B: ozonator; C: ozone analyzer; D: plug flow reactor; E: batch reactor; F: flow meter; G: dry ice trap; H: potassium iodide trap; c: cooling water; g: gas; m: liquid material.

For reactions in the methanol system, 500 g of FAMES, 1000 g of methanol and 0.25 wt% (of FAMES) sodium methoxide were added together to be supplied to the plug flow reactor by a peristaltic pump with a flow rate of 10 ml/min. For reactions in the water system, the ratio between FAMES and water was the same as the methanol system

(excluding the catalyst) and the liquid mixture flow rate was also 10 ml/min. Products were collected after 15 min counting from the first drop of liquid coming out the reactor when it reached steady state.

2.2.3 Oxone treatment

As shown in the reaction mechanism (Figure 2.3), ozonolysis products formed in methanol system consist of both aldehydes and methyl esters, where aldehydes are dominant products. The target products in this process are methyl esters, thus a further oxidation step is needed to convert the aldehydes into esters. The oxidant chosen to accomplish the goal is Oxone. Oxone is a trade name for the triple potassium salt Potassium peroxymonosulfate ($2\text{KHSO}_5 \cdot \text{KHSO}_4 \cdot \text{K}_2\text{SO}_4$) produced by DuPont. Figure 2.6 shows that the formyl group is oxidized to carboxyl group by combining one oxygen atom which originally connected to sulfur in Oxone. Due to the generation of KHSO_4 , H_2SO_4 and water as byproducts during the reaction, the pH value is usually reduced to 2-3 after the reaction is complete.

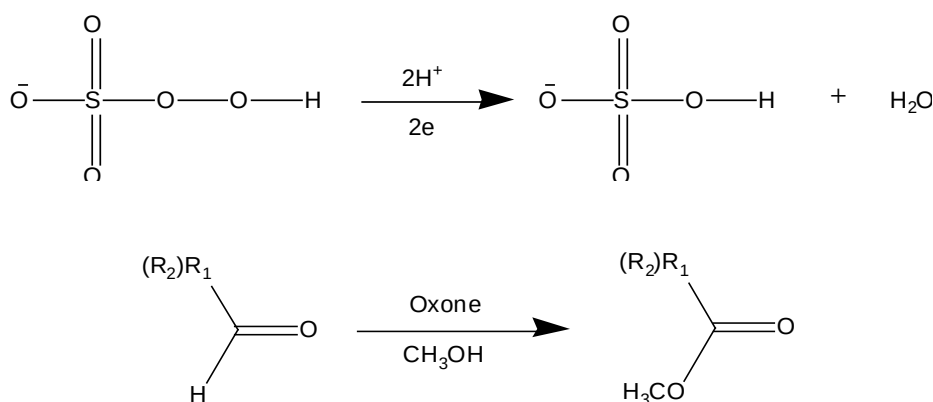


Figure 2.6 Oxone oxidation reaction mechanisms.

The reasons for choosing Oxone as the oxidant are as follows: firstly, unlike other water soluble oxidants (e.g. hydrogen peroxide), Oxone is distributed in the solution as solid suspension, due to the fine particle size, it contacts with organic compounds better than liquid-liquid system; secondly, Oxone is relatively cheap compared to other strong reactants; thirdly, the separation of final products is simple – the main byproduct is potassium salt which precipitates to the bottom of the vessel, and can be filtered out easily; trace of dissolved salt and sulfuric acid can be further removed by extraction of the products.

Oxone was added to the sample immediately after ozonation, with amount of 50% with respect to the mass of FAMES. At room temperature, the reaction was maintained for 72 hours under constant stirring.

2.2.4 GC analysis

To quantify the composition of reactant material as well as the products, GC analysis was conducted in a GC-2010 Plus gas chromatograph made by Shimadzu. This machine was equipped with a Shimadzu SHRXI-5MS capillary column (15m×0.25mm×0.25μm, -60°C~330/350°C) and an FID detector. Helium was used as carrier and makeup gas at a flow rate of 30 mL/min. H₂ and air were maintained at 40 mL/min and 400 mL/min respectively. The injector and detector were set up at 250 °C, and the column temperature started at 50 °C holding for 2 mins and then increased at the rate of 10 °C/min to 250 °C and then held for 5 mins. The injection volume of each sample was 1.0 μL with a split ratio of 70. This method was applied to the analysis of FAMES, the products after ozonolysis and the mixture after Oxone treatment.

2.2.5 GC-MS analysis

A JEOL AX-505H double-focusing mass spectrometer (JEOL, USA) was connected to a Hewlett-Packard 5890J gas chromatograph used to detect the ionized molecules of selected samples. A DB-WAX (the stationary phase is polyethylene glycol) capillary polar column (30m×0.25 mm×0.20 μm) from Restek Corporation (Bellefonte, PA) was installed to separate the aldehydes, short-chain esters and fatty esters compounds. Column temperature was started from 50 °C holding for 2 mins, and then increased with a rate of 10 °C/min to a final 250 °C, and it was kept for another 2 mins. An ionization voltage of 70 eV over the mass range of 45-500 amu was used to break the molecules into ionized fragments. Helium was chosen as carrier gas and the injection volume of each sample was 1.0 μL with a split ratio of 200. The injector temperature was 250 °C, with interface and ion source temperature maintained at 240 °C and 200 °C, respectively. A NIST/EPA/NIH Mass Spectral Library databank was used to search and identify compounds.

2.3 Results and Discussion

2.3.1 Composition of reactants and products

Compositions of FAMEs produced from different vegetable oils can vary significantly. In this project the FAMEs used were prepared from soybean oil. To eliminate the experimental error caused by the inconsistency of FAMEs content, all the FAMEs samples were prepared from the same batch provided by Zeeland Inc. and analyzed by GC in triplicates.

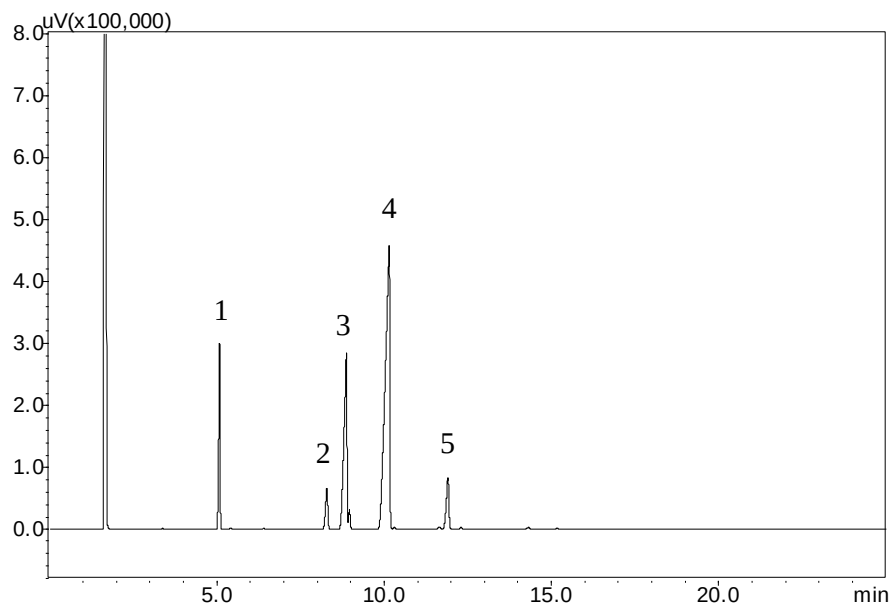


Figure 2.7 GC chromatograph for soybean oil FAMES. 1: Methyl palmitate (C16:0); 2: Methyl Stearate (C18:0); 3: Methyl oleate (C18:1); 4: Methyl linoleate (C18:2); 5: Methyl linolenate (C18:3).

From Figure 2.7, the five main compounds in soybean FAMES can be easily observed, with methyl palmitate (C16:0) as the most volatile and methyl linolenate (C18:3) as the least volatile. In ozonolysis reaction, only the three unsaturated methyl esters react with ozone. According to Table 2.1, the three components have mass fraction of 22.85%, 54.66% and 5.89% respectively. The saturated esters C16:0 and C18:0 will remain the same before and after reaction and thus act as perfect internal standards for yield calculations. Other components take up 3.36wt% of the total FAME and consist of minor fatty acid methyl esters and some other types of compounds [64].

Table 2.1 Compositions of FAMES

Component	Peak No.	wt%	mol%*
C16:0	1	9.59	10.35
C18:0	2	3.66	3.58
C18:1	3	22.85	22.52
C18:2	4	54.66	54.24
C18:3	5	5.89	5.88
Others	--	3.36	3.43

*Molecular mass of soybean FAMES was assumed as 292.2 g/mol

Ozone breaks olefinic bonds while generating formyl groups and carbonyl groups. The reaction products are mainly dependent on the position of the double bonds in the reactants. Different solvent can also lead to different compositions of products. In water system, the main products were aldehydes and trace amount of acids, while in methanol system both aldehydes and a little amount of methyl esters were formed. According to the reaction shown in Figure 2.3 and Figure 2.4, there is one main common product derived from all the three unsaturated esters, i.e. dimethyl azelate in methanol system and methyl 9-oxononanoate in water system, because all of the three compounds form a C9 chain after being broken by ozone. All the mass spectra were identified and compared with the NIST databank. The mass spectra results showed very high (mostly higher than 90%) reliability (Table 2.2) for most of the products detected after ozonolysis reaction in both

ethanol and water system. Some small compounds were not detected either due to its high volatility or low quantity (like propanal and methyl propanoate).

Table 2.2 Identification of ozonolysis products formed in ethanol and water system, with respective mass spectra reliability according to NIST databank.

No.	Ozonolysis Product	Reactant resource	Molecular formula	Reliability (%) (GC-MS)
1	Propanal	C18:3	C ₃ H ₆ O	N/A*
2	Methyl Propanoate	C18:3	C ₄ H ₈ O ₂	N/A*
3	Dimethyl Malonate	C18:3	C ₅ H ₈ O ₄	91
4	Hexanal	C18:2	C ₆ H ₁₂ O	94
5	Methyl 3,3-dimethoxypropionate	C18:3	C ₆ H ₁₂ O ₄	78
6	Methyl Hexanoate	C18:2	C ₇ H ₁₄ O ₂	91
7	Nonanal	C18:1	C ₉ H ₁₈ O	97
8	Methyl Nonanoate	C18:1	C ₁₀ H ₂₀ O ₂	94
9	Methyl 9-oxononanoate	C18:1, C18:2, C18:3	C ₁₀ H ₁₈ O ₃	91
10	Dimethyl Azelate	C18:1, C18:2, C18:3	C ₁₁ H ₂₀ O ₄	91
11	Methyl Palmitate	Unreacted	C ₁₇ H ₃₄ O ₂	99
12	Methyl Stearate	Unreacted	C ₁₉ H ₃₈ O ₂	99

* Not observed in GC chromatogram

2.3.2 Effective carbon number method for quantitative GC-FID analysis

The response factor for GC analyses using FID is crucial for calculating analyte concentration. Usually, absolute response factor (Equation 2.1) is acquired through the calibration curve made from a series of standard solutions of known concentration; however, if pure sample for certain compound is not available, a relative response factor can provide concentration estimations (Equation 2.2 and Equation 2.3). One of the convenient methods of calculating relative response factor is using effective carbon number (ECN).

$$RF = A_{comp} / C_{comp} \quad (\text{Equation 2.1})$$

$$RF' = \frac{A_{comp} C_{ref}}{A_{ref} C_{comp}} \quad (\text{Equation 2.2})$$

$$RF' = \frac{ECN_{comp} MW_{ref}}{ECN_{ref} MW_{comp}} \quad (\text{Equation 2.3})$$

Table 2.3 Contributions to the Effective Carbon Number

Atom	Type	ECN contribution
C	Aliphatic	1
C	Aromatic	1
C	Olefinic	0.95
C	Acetylenic	1.3
C	Carbonyl	0
C	Carboxyl	0
C	Nitrile	0.3
O	Ether	-1
O	Primary alcohol	-0.5
O	Secondary alcohol	-0.75
O	Tertiary alcohol	-0.25
N	Amine	As 0 in alcohols
Cl	2+-Aliphatic	-0.12 per chlorine
Cl	On olefinic C	0.05

The concept of ECN was originally published to explain flame ionization responses obtained from the analysis of isomeric or homologous series of organic compounds [65]. As displayed in Table 2.3 [63], some atoms appeared in different groups will give different ECN contribution. For example, a carbon in acetylenic group has the highest ECN contribution of 1.3, while an oxygen atom in ether will give an ECN contribution as low as -1. Based on Equation 2.3, the relative response factor can be calculated by known ECN for both new compound and reference compound.

By applying the data in Table 2.3, the ECN values for all the main compounds in this project were calculated and shown in Table 2.4 and corresponding ECN/MW were given in the next column. With reference to Equation 2.3, given a reference compound, the relative response factor for a new compound is calculated by dividing the ECN/MW value of the new compound by the ECN/MW value of reference compound. To evaluate the accuracy of this method, the relative response factor from experimental results were compared with the theoretical values in Table 2.5. Among the 6 compounds (hexanal, methyl hexanoate, nonanal, methyl nonanoate, dimethyl azelate and methyl palmitate) chosen for comparison, the biggest error corresponded to methyl hexanoate which was 12.9% and the lowest error was associated to methyl palmitate with the value of 1.02%.

Table 2.4 Calculated Effective Carbon Numbers for main compounds

Compound	Molecular Formula	MW (g/mol)	ECN	ECN/MW
Methanol	CH ₄ O	32.04	0.52*	0.01623
Hexanal	CH ₃ (CH ₂) ₄ CHO	100.16	5	0.04992
Hexanoic acid	CH ₃ (CH ₂) ₄ COOH	116.16	5	0.04304
Methyl hexanoate	CH ₃ (CH ₂) ₄ COOCH ₃	130.2	5.5	0.04224
Nonanal	CH ₃ (CH ₂) ₇ CHO	142.24	8	0.05624
Nonanoic acid	CH ₃ (CH ₂) ₇ COOH	158.23	8	0.05056
Methyl 3,3-dimethoxypropionate	(CH ₃ O) ₂ CHCH ₂ CO ₂ CH ₃	148.16	2.5	0.01687
Methyl nonanoate	CH ₃ (CH ₂) ₇ COOCH ₃	172.3	8.5	0.04933
Dimethyl Malonate	CH ₃ OOCCH ₂ COOCH ₃	132.11	2	0.01514
Methyl 9-oxononanoate	CH ₃ OOC(CH ₂) ₇ CHO	186.25	7.5	0.04027
Monomethyl azelate	CH ₃ OOC(CH ₂) ₇ COOH	202.25	7.5	0.03708
Dimethyl azelate	CH ₃ OOC(CH ₂) ₇ COOCH ₃	216.3	8	0.03699
Methyl palmitate	CH ₃ (CH ₂) ₁₄ COOCH ₃	270.5	15.5	0.05730
Undecanedioic acid,1-methyl ester	CH ₃ OOC(CH ₂) ₉ COOH	230.3	9.5	0.04125
Methyl stearate	CH ₃ (CH ₂) ₁₆ COOCH ₃	298.5	17.5	0.05863

* According to [66]

With the application of ECN method, concentration for all the compounds that were indicated in GC chromatogram could be calculated. As a result, the yields for the main products could be obtained, taking methyl stearate as the internal standard to estimate the original amount of FAMES reacted.

Table 2.5 Comparison between experimentally obtained ECN and calculated ECN

Compound	Relative factor (experiment)	Relative factor (calculated)	Error ^(a) (%)
Hexanal	0.7834	0.8515	+8.69
Hexanoic acid ^(b)	--	0.7342	--
Methyl hexanoate	0.8273	0.7205	-12.90
Nonanal	0.8887	0.9593	+7.95
Nonanoic acid ^(b)	--	0.8623	--
Methyl 3,3-dimethoxypropionate ^(b)	--	0.2878	--
Methyl nonanoate	0.8983	0.8415	-6.33
Dimethyl Malonate ^(b)	--	0.2582	--
Methyl 9-oxononanoate ^(b)	--	0.6869	--
Monomethyl azelate ^(b)	--	0.6324	--
Dimethyl azelate	0.6906	0.6309	-8.64
Methyl palmitate	0.9675	0.9774	+1.02
Undecanedioic acid,1-methyl ester ^(b)	--	0.7036	--
Methyl stearate	1	1	--

(a) Obtained by dividing absolute value of difference between experimental relative factor and calculated relative factor by experimental relative factor;

(b) Commercial standard sample is not available

2.3.3 Ozonolysis in methanol system

The profile for ozonolysis products in methanol system is shown in Figure 2.8. As estimated by the height of the peaks, the main outputs are aldehydes with only very little

amount of esters formed (Table 2.6). The sum of the molar yields of ester and aldehydes derived from ozonolysis of methyl oleate (C18:1) show a relatively good molar balance closure, indicating that approximately 49% of the double bonds were cleaved during ozonolysis. The selectivity of this reaction was more favorable toward aldehyde formation than ester formation in both sides of the double bond. Similarly, a very small molar yield of methyl hexanoate ester (3.5%) was also achieved by ozonolysis of methyl linoleate, compared to the aldehyde product hexanal (32.74%). The C3 product of this reaction is highly volatile and could not be recovered for this study.

Even though the molar yields are lower than 50 % for the ozonolysis products, there was no evidence of the presence of any unreacted unsaturated FAMEs, suggesting the presence of ozonides or other derivatives that could not be detected by the GC method used in this study. This implies that the fresh product solution after ozonolysis should be taken care of with caution as it might contain high amount of unstable ozonides.

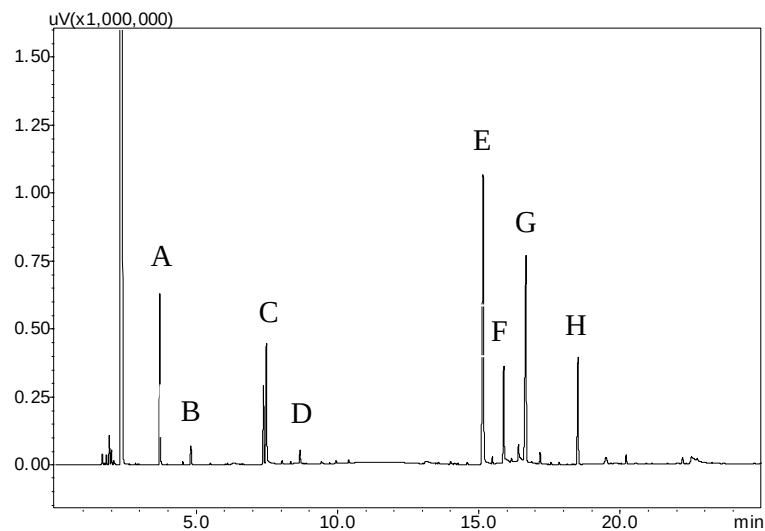


Figure 2.8 Chromatogram for products from ozonolysis in methanol system. A: Hexanal; B: Methyl hexanoate; C: Nonanal; D: Methyl nonanoate; E: Methyl 9-oxononanoate; F: Dimethyl azelate; G: Methyl palmitate; H: Methyl stearate.

Table 2.6 Yield for products from ozonolysis in methyl system

Compound	Yield (%)
Hexanal	32.74
Methyl hexanoate	3.50
Nonanal	45.44
Methyl nonanoate	3.59
Methyl 9-oxononanoate	39.53
Dimethyl azelate	10.13
Methyl palmitate	Unreacted
Methyl stearate	Unreacted

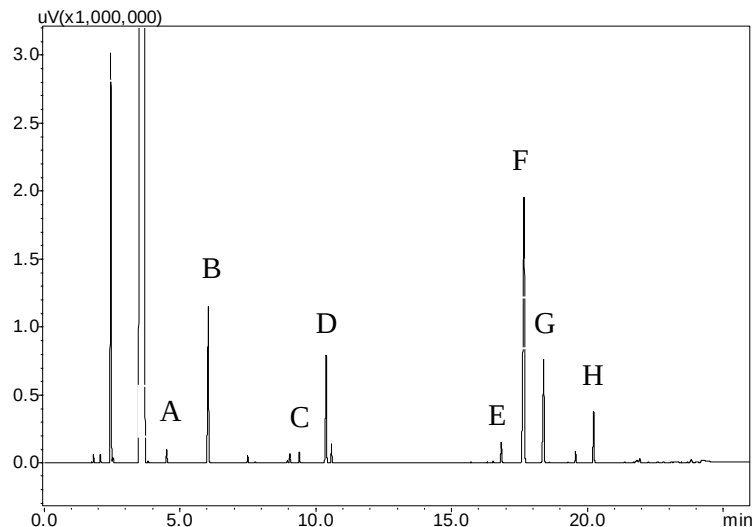


Figure 2.9 Chromatogram for products after oxone treatment. A: Hexanal; B: Methyl hexanoate; C: Nonanal; D: Methyl nonanoate; E: Methyl 9-oxononanoate; F: Dimethyl azelate; G: Methyl palmitate; H: Methyl stearate.

In order to convert the aldehydes to methyl esters, Oxone was added to the solution immediately after ozonolysis. After 72 hours of reaction under constant stirring, the main products changed from aldehydes to methyl esters as shown in Figure 2.9. The yield in Table 2.7 also indicated that most of aldehydes have been converted to esters. For example, the yield of Methyl 9-oxononanoate was only 4.39% in contrast with 72.38% for the yield of dimethyl azelate after Oxone workup. Some acids were also detected as byproducts, and this may be due to the existence small amounts of water generated from Oxone oxidization according to Figure 2.6. The summation of yield for compounds derived from the same reactant is slightly smaller than 100%. This may indicate that some intermediate products (e.g. ozonides) didn't decompose completely and could not

be detected by GC or could also be partially attributed to uncertainties in the quantification method, notably ECN.

Table 2.7 Yield for products after Oxone treatment

Compound	Yield (%)
Hexanal	5.40
Hexanoic acid	7.32
Methyl hexanoate	65.12
Nonanal	7.61
Nonanoic acid	6.93
Methyl nonanoate	70.12
Methyl 9-oxononanoate	4.39
Monomethyl azelate	8.77
Dimethyl azelate	72.38
Methyl palmitate	Unreacted
Methyl stearate	Unreacted

2.3.4 Ozonolysis in water system

Reaction in water system shows a significantly different profile in terms of the types of products compared to the methanol system, as displayed by the GC chromatogram in Figure 2.10. Firstly, the peaks are clearer and not many small peaks are shown, indicating that there is less formation of byproducts. Secondly, the peaks are “taller” compared to the peaks for the same compounds in methanol system, using methyl stearate peak as the reference. This can be more obviously seen in Table 2.8. The yields for the three

aldehydes are significantly higher. The byproducts are also different from those in methanol system after Oxone treatment, as only acids were generated instead of esters. This result was expected, because there was no alcohol in the solvent to promote esterification.

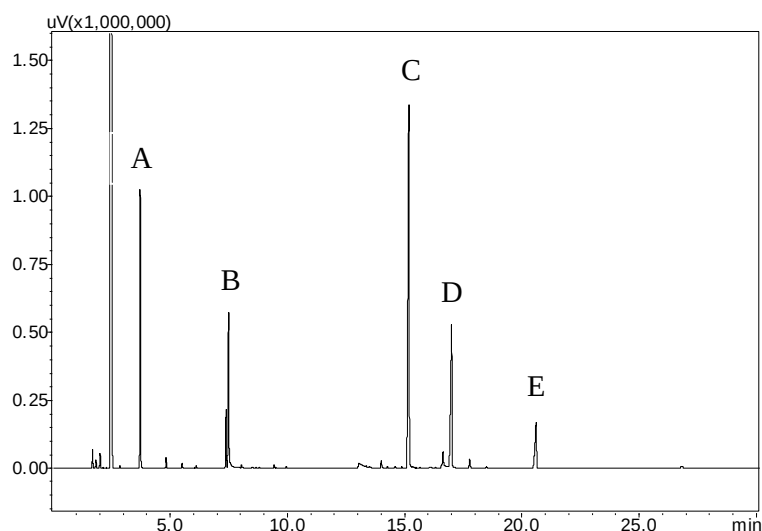


Figure 2.10 Chromatogram for products of ozonolysis in water system. A: Hexanal; B: Nonanal; C: Methyl 9-oxononanoate; D: Methyl palmitate; E: Methyl stearate.

Another clear difference between the water system and methanol system is that the summation of the yield for products derived from the same reactant is much higher with respect to the products from ozonolysis in methanol before Oxone treatment. This indicates that water system is more effective in completing the cleavage of the double bonds, quickly decomposing ozonides (or any other intermediate compounds) and therefore it can help reduce the potential hazard during reaction. This factor is extremely important, especially when designing processes for industrial applications.

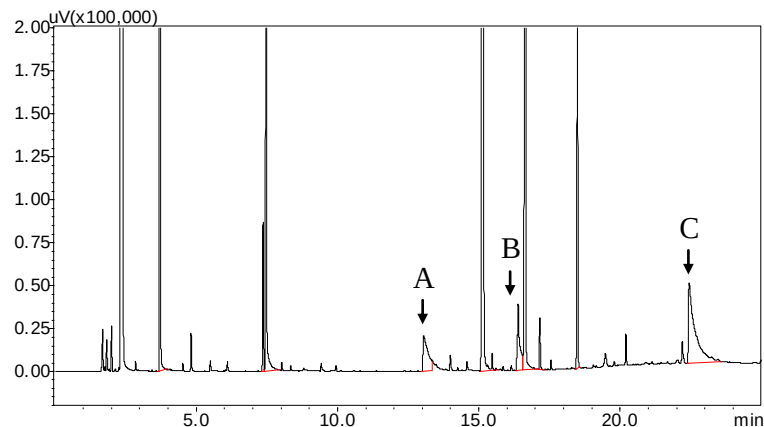


Figure 2.11 Chromatogram for acid products of ozonolysis in water system. A: Hexanoic acid; B: Nonanoic acid; C: Monomethyl azelate

The peaks for acids cannot be seen from Figure 2.10, however, by enlarging the chromatogram, the three broad peaks for hexanoic acid, nonanoic acid and monomethyl azelate can be easily identified (Figure 2.11). The yield of these acid byproducts can be highly affected by the retention time of the reaction, which means, more acid tends to be generated if the time for reactants contact with ozone is increased. A trade-off between the conversion of the reactants and the generation of byproducts should be made to optimize the reaction for achieving the highest possible yields of the desired compounds.

Table 2.8 Yield for products from ozonolysis in water system

Compound	Yield (%)
Hexanal	62.14
Hexanoic acid	8.34
Nonanal	70.11
Nonanoic acid	7.85
Methyl 9-oxononanoate	66.53
Monomethyl azelate	9.89
Methyl palmitate	Unreacted
Methyl stearate	Unreacted

The overall mass yields of main products from ozonolysis in methanol (after Oxone treatment) and in water were compared in Table 2.9. In terms of mass, the aldehyde products obtained from water system were about 20% to 30% less than the corresponding methyl ester products from methanol system, this was due to 1) the molecular weights of aldehydes are lower than corresponding methyl esters, 2) the molar yield of aldehydes were also lower than methyl esters derived from the same unsaturated FAMES. For example, the molar yield of hexanal was 62.14% and methyl 9-oxononanoate was 66.53%; while the molar yield of methyl hexanoate and dimethyl azelate were 65.12% and 72.38% respectively. One reason for this may be that in water system, since the reaction happened in two phases, some aldehyde products may have dissolved in water phase and therefore were lost. Another reason might be that more acids were generated and also dissolved in water phase.

Table 2.9 Mass yield of products from ozonolysis in two systems

Methanol system		Water system	
Product	Mass yield (Kg/100 Kg FAMES)	Product	Mass yield (Kg/100 Kg FAMES)
Methyl hexanoate	15.74	Hexanal	11.55
Methyl nonanoate	9.31	Nonanal	7.69
Dimethyl azelate	44.28	Methyl 9-oxononanoate	35.04
Methyl palmitate	9.58	Methyl palmitate	9.58
Methyl stearate	3.66	Methyl stearate	3.66

2.4 Conclusions

The chapter reviewed the background for ozone chemistry, ozonolysis on fatty acid groups and ozonolysis conducted on soybean-oil FAMES. Analytical method GC-FID and GC-MS were introduced to determine the composition of soybean-oil FAMES and the respective products of ozonation in methanol and water system. The effective carbon number (ECN) method, as an estimation for compounds that do not have commercial standards available, was proposed and implemented. The good reliability of this method was proved by comparing the calculated relative response factors with known experimental data.

Ozonolysis were carried out in both methanol and water system and, for each system, a continuous process was applied. The GC-MS results showed that the products given by ozonolysis in methanol are highly consistent with the anticipated outputs derived based on the reaction mechanism. The GC-FID analysis indicated that the conversion of the

three unsaturated esters in FAMES was 100% in all the reactions. The yields for the main compounds in each process were also calculated. The products obtained from ozonolysis in methanol after Oxone treatment were methyl esters with yields between 65% and 73%. The products formed from ozonolysis in water were mainly aldehydes and the yields fell between 62% and 71%.

On average, the unknown compounds are around 10% of the products for both of the reactions in two systems. The fact that the mass balance did not close for the ozonolysis reactions performed in this study, implies that undetected ozonides formed during ozonolysis in both systems may not be completely decomposed to product. Also, this observation could also be partially attributed to the uncertainties in the GC quantification method by ECN.

Chapter 3: Mass Transfer and Reaction Kinetics Study for Ozonation of FAMES

3.1 Introduction

In the previous chapter we mainly focused on identifying the products of ozonolysis of soybean-oil FAMES. In this chapter, we will study the mass transfer and reaction kinetics parameters that govern this reaction, as well as the impact of processing conditions on its efficiency.

The ozonolysis of FAMES conducted in both methanol and water are heterogeneous reactions. A heterogeneous reaction is one that takes place between two or more distinct states of matter. In the case of this study, the methanol reaction system contains a liquid and a gaseous phase, and the water reaction system consists of two immiscible liquid phases (aqueous and organic) and a gaseous phase. One of the key characteristics of a heterogeneous reaction is that it can only take place where the surfaces of the different states of matter are in contact. Because of this property, the rate of heterogeneous reactions is usually controlled by two factors: the mass transfer of one matter going through the other and the reaction kinetics. In such circumstances, either factor can be the limiting step of reaction.

Mass transfer of ozone in aqueous system has been extensively studied due to the wide application of ozone in wastewater treatment [67]. In 1970, it was found that the mass transfer of ozone was controlled within a liquid film closely adjacent to the gas-liquid interface, and therefore the overall mass transfer coefficient could be approximated to the local liquid mass transfer coefficient [68]. Furthermore, the liquid-side overall mass transfer coefficient (k_La) was measured in a contactor equipped with a gas sparger [69]

and a mathematical model related to the gas flow rate was developed. Similar mass transfer studies were also performed for drinking water treatment [70, 71]. Correlations between k_La values and the superficial gas velocity for the design and operation of fine bubble ozone contactors were established [72] and supported [73, 74]. These correlations combined with ozone decay kinetics have also been incorporated into various hydrodynamic models to describe ozonation processes [75, 76]. Additionally, it was found that reactions of ozonolysis may accelerate the mass transfer of ozone from gas phase into liquid phase [68]. To explain this phenomenon, two general kinetic mechanisms were proposed including 1) slow kinetic regime and 2) fast kinetic regime, depending on the relative rates of ozone physical absorption to ozone chemical reactions. It was stated that the slow kinetic regimes occur when the ozonolysis reactions are slower and the reaction only reduced the concentration of dissolved ozone in the bulk liquid. For higher rate of reactions, the mass transfer of ozone may occur in the fast kinetic regime. When this happens, dissolved ozone is completely depleted within the liquid film adjacent to the gas-liquid interface. The apparent rate of ozone mass transfer may even exceed the maximum rate of gas-liquid mass transfer of ozone. An enhancement factor “E” was defined as the actual rate of mass transfer with ozone reactions divided by the maximum rate of physical absorption without any reaction [77]. To demonstrate the enhancement of the presence of chemical reactions on ozone gas-liquid mass transfer, three types of water samples, including deionized water, tap water and pulp mill effluents were investigated by Zhou et al. [67].

In previous reports, the mass transfer of ozone in aqueous solutions has been the focus of theoretical and practical interest, however this interest is not observed for ozonolysis in

organic solvents. Despite the solubility of ozone in water and other organic solvents was studied [78, 79], no previous work has been reported about solubility of ozone in methanol.

Besides mass transfer, reaction kinetics is also an important factor in heterogeneous systems. However, reaction kinetics of ozonolysis on fatty acids esters has not been extensively studied in the literature compared to the large amounts of reports on ozone mass transfer. While most researchers were focusing on the analysis of products under different reaction conditions [80, 81], some general examinations on ozonolysis kinetics of fatty acid derivatives were reported without calculating the reaction rate parameters [56]. One of the few thorough reports in this field can be found in a manuscript about aerosols, where ozonolysis of methyl oleate monolayers at the air-water interface was carried out and a second order reaction model was established, with a reaction rate parameter of $(5.7 \pm 0.9) \times 10^{-10} \text{ cm}^2 \text{ molecule}^{-1} \text{ s}^{-1}$ [82].

In this project we applied the theory of number of transfer units (NTU) into mass transfer study of ozone in methanol and water. This theory is usually used for gas-liquid absorption column mass transfer calculation. By applying this model, the reactor system is simplified and the number of parameters related to the mass transfer coefficient equation is also reduced. The limitation of this model is that the mass transfer coefficient obtained from this study is applicable for the specific reactor in use. Also, we only focused on the ozone mass transfer in a pure solvent without considering the reaction kinetics, assuming mass transfer is the limiting step of reaction as an approximation for the ozonolysis model. The goal of the study is to evaluate the performance of FAME

ozonolysis in methanol and provide some preliminary data for reactor design which may be useful for scale-up production in the future, given a similar reaction system.

The apparent reaction kinetics for ozonolysis in both methanol and water solvent systems was also examined, which included the combined effect of mass transfer and reaction kinetics. This part of the study focused on ozonolysis in batch and continuous reactions, which were conducted for both solvent systems. The effect of temperature was studied in batch reactions with methanol and water as solvents, while the effect of pH was also evaluated for the aqueous system. For the continuous reaction, the impact of flow rate of reactants on the reaction rate was determined for both solvents.

Oxone treatment after ozonolysis in methanol was carried out using batch and fed-batch strategies to evaluate their impact on the oxidation of aldehydes formed during ozonolysis in methanol. Optimal reaction conditions determined by the overall results of this study for both solvent systems will be recommended.

3.2 Experiment

3.2.1 Ozone measurement

The main equipment used for ozone concentration measurement was a Unico 2800 UV-vis spectrophotometer. Direct measurement method was applied to determine the concentration of ozone in solvent (water or methanol), in which the absorbance value under ultra-violet light at 258 nm wave length was measured and converted to concentration by using an extinction coefficient of $3,000 \text{ M}^{-1}\text{cm}^{-1}$ [83]. To maintain the linear correlation between the absorbance and concentration, the original solution was

diluted 50 times in order to achieve absorbance values between 0 and 1.0. In each measurement, the same blank solvent was used as the control sample.

Ozone concentration in the gaseous phase was measured with two methods. The simpler method was by direct analysis using a Mini-Hicon ozone analyzer. However, the drawback of this instrument is that it is sensitive to other chemical vapors and therefore, it is not proper for accurate outlet gas measurement. The secondary method used was the modified indigo method. Indigo solution was prepared based on a standard published in 1981 [84]. The indigo reagent (I) could be used in this study because the ozone concentration in the experiments was around 5-10 wt%. The measurement was performed by adding 20 ml of indigo reagent into a 30 ml cuvette, sealed with a rubber cap, followed by adding 5 ml of a gas sample collected with a syringe. After gentle agitation for 1 min, the reagent solution was measured in the UV-vis spectrophotometer under 600 nm wave length with original indigo reagent as reference. The absolute value of the absorbance was recorded for calculating ozone concentration using the following equation:

$$mg\ O_3 / L = \frac{100 \times \Delta A}{f \times b \times V} \quad (\text{Equation 3.1})$$

where:

ΔA = difference in absorbance between sample and blank,

b = path length of cell, cm,

V = volume of sample, mL (normally 90 mL), and

$f = 0.42$.

3.2.2 GC analysis

The GC equipment and analysis method are as described in 2.2.4.

3.2.3 Ozonolysis reaction

In the batch reactions, ozone was produced by a CFS-3A ozone generator from Ozonia North America LLC. Oxygen/Ozone gas mixture flow rate was 1 L/min, with a weight fraction of 10% ozone. Compressed oxygen was used as input gas to generate ozone.

The reactor was modified from a dry ice trap cylinder with diameter of 3.8 cm and length of 32 cm. The inlet gas was injected in the reactor through a deep-tube, submerged into the liquid-phase during reaction. The deep-tube was equipped with a spray nozzle on the tip to create small bubbles and increase the mass transfer efficiency during reaction. During reaction, the outlet gas passed through a KI solution (1M), to trap the unreacted ozone. The reaction was conducted independently using either methanol or water as solvents. In methanol, 20 g of FAMES, 40 g of methanol and 0.25 wt% sodium methoxide (based on the added FAMES) were added into reactor. In water system, the reactants consisted of 20 g of FAME and 40 g of water without any added catalyst. The reaction duration time was between 45 minutes to 1 hour under temperature controlled conditions by cooling water. The continuous reaction was performed as described in 2.2.2.

3.2.4 Ozonolysis of FAMES in methanol

Ozonolysis was conducted in both batch and continuous reactors. In batch reactor, the cooling condition was varied as under room temperature ($\sim 22\text{ }^{\circ}\text{C}$), ice bath ($\sim 0\text{ }^{\circ}\text{C}$) and

dry ice bath ($\sim -75\text{ }^{\circ}\text{C}$). In continuous reactor, the cooling system was constantly flowing water with change of flow rate of material from 3 to 27 ml/min.

3.2.5 Ozonolysis of FAMES in water

Ozonolysis in water was similar to ozonolysis in methanol and the reaction details are also shown in 2.2.2 and 3.2.2. The difference between ozonation reaction in water and in methanol are the following: 1) in methanol system, 0.25 wt% of sodium methoxide was added as catalyst while in water solvent no other chemical was introduced except for FAMES and water; 2) the FAMES-to-solvent mass ratio in water system was 1:3 while in methanol system was 1:2 for both of the two reaction conditions. Based on preliminary data, the effect of FAMES-to-solvent mass ratio was not significant to the reaction rate, however, the reason we chose different mass ratio in water system was mainly based on safety considerations, because more water will absorb more heat generated by the reaction, and also based on the fact that more water will provide better emulsification as the reactants were in two phases.

3.2.6 Mass transfer model of ozone in methanol and water

The mass transfer study of ozone in customized plug flow reactor was conducted based on the method of transfer units, which is usually applied in mass transfer studies for gas-liquid absorption columns. The biggest difference that needs to be noticed is that in absorption columns, the gas flow and liquid flow are usually countercurrent, however, in our model the mass transfer happens in concurrent flow, since both gas and liquid reactants enter into the reactor from the same side.

In this method, the height of packing in the column (in our case, the length of reactor) can be evaluated either based on the gas phase or the liquid phase using the following formula:

$$Z = NTU \times HTU \quad (\text{Equation 3.2})$$

where,

Z = the length of the reactor, m

NTU = the number of transfer units, dimensionless

HTU = the height of transfer units, m

NTU is the theoretical number of trays required for a trayed column in the absorption column calculation. Similarly, here NTU can be considered as the theoretical number of unit length of the PFR reactor. The height of a transfer unit (HTU) can be considered as the unit length of the reactor for mass transfer.

For gas-liquid mass transfer, Equation 3.2 can be applied to both liquid and gas phases, and the calculated value for reactor length Z will be the same, which can be expressed as $Z = NTU_{\text{gas}} \times HTU_{\text{gas}} = NTU_{\text{liquid}} \times HTU_{\text{liquid}}$. In this project, we mainly studied the mass transfer in gas phase, since we assumed that with ozonolysis reaction, the mass transfer in liquid phase will be much faster compared to gas phase, thus the mass transfer efficiency in gas phase will determine the overall speed.

The model is described by these equations combined with Equation 3.2:

$$(y - y^*)_{LM} = \frac{(y^o - y^{o*}) - (y^e - y^{e*})}{\ln\{(y^o - y^{o*})/(y^e - y^{e*})\}} \quad (\text{Equation 3.3})$$

$$NTU_{gas} = \frac{(y^o - y^e)}{(y - y^*)_{LM}} \quad \text{(Equation 3.4)}$$

where:

NTU_{gas} = Gas phase number of transfer units

y = Mole fraction of ozone

y^* = Mole fraction of ozone in equilibrium with liquid flow

y^o = Mole fraction of ozone in inlet gas flow

y^{o*} = Mole fraction of ozone in equilibrium with inlet liquid flow (=0)

y^e = Mole fraction of ozone in outlet gas flow

y^{e*} = Mole fraction of ozone in equilibrium with outlet liquid flow

Similarly, the equations for liquid phase mass transfer calculation are shown as follows:

$$(x^* - x)_{LM} = \frac{(x^{o*} - x^o) - (x^{e*} - x^e)}{\ln\{(x^{o*} - x^o)/(x^{e*} - x^e)\}} \quad \text{(Equation 3.5)}$$

$$NTU_{liquid} = \frac{(x^o - x^e)}{(x - x^*)_{LM}} \quad \text{(Equation 3.6)}$$

where:

NTU_{liquid} = Liquid phase number of transfer units

x = Mole fraction of ozone

x^* = Mole fraction of ozone in equilibrium with gas flow

x^o = Mole fraction of ozone in inlet liquid flow (=0)

x^{o*} = Mole fraction of ozone in equilibrium with inlet gas flow

x^e = Mole fraction of ozone in outlet liquid flow

x^{e*} = Mole fraction of ozone in equilibrium with outlet gas flow

After NTU_{gas} is calculated, inputting into Equation 3.2, HTU_{gas} can also be calculated.

To further determine the gas phase mass transfer coefficient, the following equations will be used:

$$HTU_{gas} = \frac{G}{K_Y a(1-y)_{LM}^*} \quad (\text{Equation 3.7})$$

$$(1-y)_{LM}^* = \frac{(1-y^o) - (1-y^{o*})}{\ln\{(1-y^o)/(1-y^{o*})\}} \quad (\text{Equation 3.8})$$

where:

HTU_{gas} = Gas phase height of transfer units

G = Gas flow rate, mol/m²s

K_Y = Overall gas-phase mass transfer coefficient, mol/m²s

a = Packing parameter, m^2/m^3

The only unknown variables are K_Y and a , and they are usually combined as a single parameter $K_Y a$ ($\text{mol}/\text{m}^3\text{s}$).

Similarly, for liquid phase, the equations turn to be:

$$HTU_{liquid} = \frac{L}{K_X a(1-x)_{LM}^*} \quad (\text{Equation 3.9})$$

$$(1-x)_{LM}^* = \frac{(1-x^o) - (1-x^{o*})}{\ln\{(1-x^o)/(1-x^{o*})\}} \quad (\text{Equation 3.10})$$

where:

HTU_{liquid} = Liquid phase height of transfer units

L = Liquid flow rate, $\text{mol}/\text{m}^2\text{s}$

K_X = Overall liquid-phase mass transfer coefficient, $\text{mol}/\text{m}^2\text{s}$

a = Packing parameter, m^2/m^3

Once the mass transfer coefficient is known, the rate of mass transfer can be calculated using this equation:

$$Q = Ka(y - y^*)V \quad (\text{Equation 3.11})$$

where:

Q = Rate of mass transfer, mol/s

K = Overall mass transfer coefficient, mol/m²s

V = Volume of reactor, m³

3.2.7 Assumptions of model and Henry's law constant measurement

By applying the above equations, we assumed that there is no decay of ozone in the whole process including both the reaction process and the measurement process. To evaluate the validity of this assumption, we took a methanol or water solution containing ozone and measured the concentration of ozone with time. The result showed that in 6 minutes the concentration of ozone dropped by less than 1.5% percent in both methanol and water solution and in 10 mins the concentration decreased less than 2.5%, which can be considered an acceptable error range. It was also assumed that oxygen does not interfere with the absorbance of ozone at 258 nm and the absorbance of ozone in water and methanol system obeys Beer-Lambert Law.

The third assumption is the solubility of ozone obeys Henry's law. In order to calculate the mole fraction of ozone in equilibrium with outlet liquid flow (y^{e*}), we need to determine Henry's law constant. In water system, the constant was calculated as 5846.7 atm/(mol fraction) through this equation [85]:

$$K_H = 3.842 \times 10^7 [OH^-]^{0.035} \exp[-2428/(T/K)] \quad (\text{Equation 3.12})$$

where:

K_H = Henry's law constant (atm/mole fraction)

$[OH^-]$ = Concentration of OH^- (mol/L)

T = Temperature (K)

In methanol system, the Henry's law constant was measured by passing ozone and oxygen gas mixture into methanol in a semi-batch reactor for more than 40 minutes until the solution was saturated with ozone (determined by measuring the change of concentration value constantly), with the overall gas pressure and ozone mole fraction known. By dividing the value of ozone partial pressure by the maximum mole fraction of ozone in solution, the average Henry's law constant was obtained as 771.17 atm/(mol fraction) which is much smaller compared to that in water system. This indicates that solubility of ozone is higher in methanol than in water given the same partial pressure and temperature.

3.2.8 Extraction of organic products from solution after Oxone treatment

Upon completion of the reaction, the excess salt from Oxone was filtered out, and the product was neutralized by adding KOH (85%) until the pH reached to 4-5. Under this pH value, the esters are relatively stable, while under higher pH we observed some decomposition of esters by analyzing with GC. More salt precipitated after the neutralization process which occurred in 1 to 2 hours. When the solution became clear, the sediment was filtered out. In order to remove the dissolved salt, extraction was carried out with hexane and water. Extractant was put directly into 10 ml sample vial with certain amount of sample, after 30 s shaking, the vial put on the bench standing for 24 hours.

Two layers formed with a clear boundary and then were separated. The organic layer was weighed and the composition was analyzed by GC. Five batches with different sample to extractant ratios were conducted, from number 1 to 5, the ratios were 4:6, 4:4, 4:3, 4:2 and 4:1. Experiments under the same condition were repeated twice and the mean value was calculated as final result.

3.3 Results and Discussion

3.3.1 Reaction kinetics of ozonolysis in methanol system

3.3.1.1 Batch process

Ozonolysis of FAMES in methanol was initially carried out in a semi-batch reactor for 45 min with continuous supply of ozone going through constant amount of reactant solution. The reaction condition was described in 3.2.3 and ice/water bath was applied to keep the reaction under lower temperature. The course of reaction was monitored by GC after every 10 mins. The GC chromatograms for the solution before and after reaction were compared in Figure 3.1. The starting material contains five peaks which are the five methyl esters derived from soybean oil, with the first two being saturated and last three being unsaturated.

When the reaction started, the last three peaks started decreasing, as only the unsaturated compounds react with ozone. At the time of 10 mins after reaction started, the only obvious peak that can be seen from the GC chromatogram was peak H which was for Methyl 9-oxononanoate. After reaction continued for another 10 mins, all the 4 main product peaks showed up and all the reactant peaks could also be observed from the

figure, however, when reaction was carried out for 30 mins, the peak for methyl linolenate almost disappeared from the chromatogram which indicated that the conversion of this compound was close to complete. By the end of reaction, all the reactant peaks disappeared from the chromatogram which means the conversions were 100% complete.

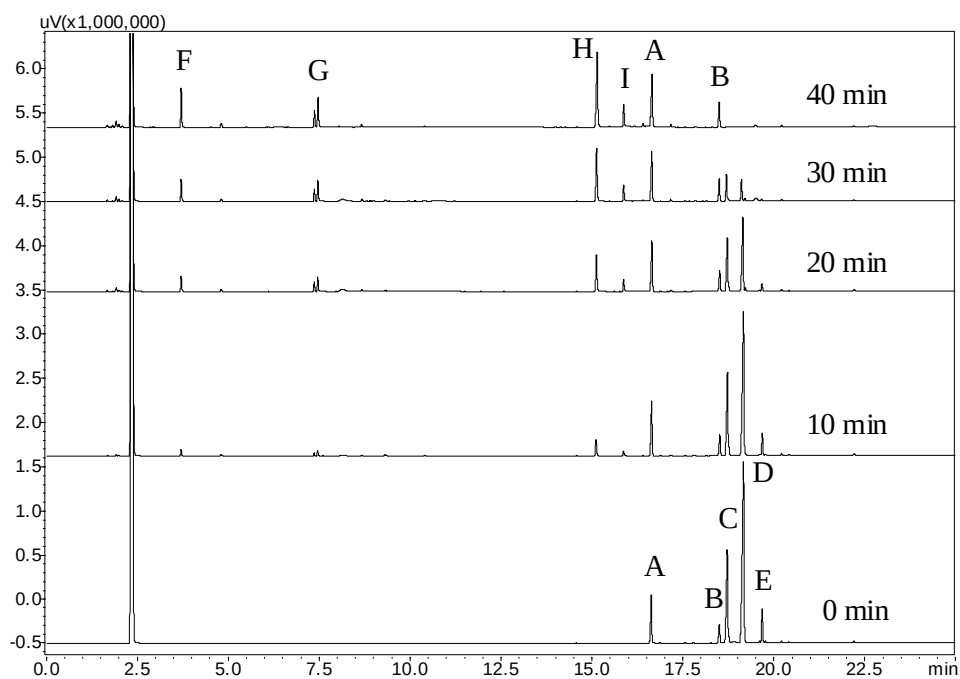


Figure 3.1 GC chromatograms for FAMES in methanol solution during ozonolysis in semi-batch reactor. Oxygen/ozone gas mixture flow rate was 1 L/min, with 10 wt% of ozone. A: Methyl palmitate; B: Methyl Stearate; C: Methyl oleate; D: Methyl linoleate; E: Methyl linolenate; F: Hexanal; G: Nonanal; H: Methyl 9-oxononanoate; I: Dimethyl azelate.

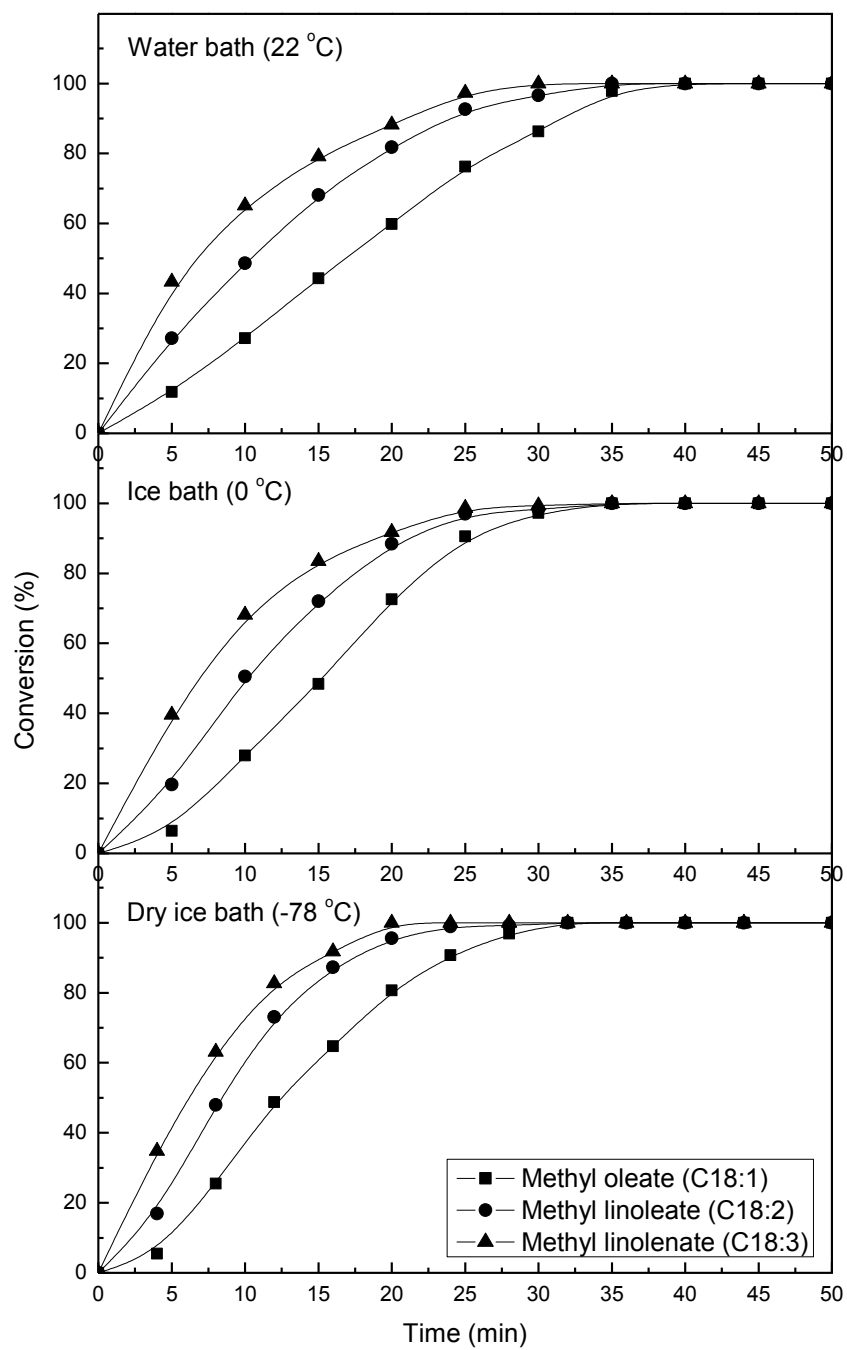


Figure 3.2 Ozonolysis of FAMES in three cooling systems using methanol as solvent system.

Ozonolysis is an exothermal reaction, thus it should be carried out at low temperatures to avoid the heat accumulation for safety concerns. To examine the effect that temperature causes on reaction rate, we conducted the reaction under three cooling regimes in a semi-batch reactor, which were room temperature, ice-water bath and dry ice-acetone bath with 22 °C, 0 °C and -78 °C at starting temperature, respectively. During the reaction, the temperature of reactants kept at room temperature conditions increased to 42-45 °C, while the other reactions occurred in ice-water bath and ice-acetone bath kept a relatively constant temperature.

Comparing the results from three conditions (Figure 3.2), it is observed that the reaction rate increases with decreasing temperature. As known, given no mass transfer obstacle, increasing the temperature usually improves reaction rate because of the increase of number of high energy collisions which lead to reaction. However, the experimental result does not follow this theory, suggesting that mass transfer is the limiting step for ozonolysis in methanol. The rate of mass transfer of ozone in methanol is proportional to the mass transfer coefficient, the difference of ozone concentration between the gas phase and equilibrium concentration in gas phase to the liquid phase, and the bubble surface area:

$$Q = K_c a \cdot (C_{O_3} - C_{O_3}^*) \cdot V \quad (\text{Equation 3.13})$$

where:

Q = Rate of mass transfer of ozone, mol/s;

$K_c a$ = Combined mass transfer coefficient, s^{-1} ;

C_{O_3} = Molar concentration of ozone in gas phase, mol/L;

$C_{O_3}^*$ = Molar concentration of ozone in equilibrium with liquid phase, mol/L;

V = Bubble size, L;

Temperature can affect all the three parameters. The input gas phase temperature is around 32 °C for all the three conditions, and gas bubble passes through the liquid in a very high speed, so we can assume that the transfer coefficient is not affected much by the liquid temperature. We assume $C_{O_3}^* = 0$ because the reaction consumes ozone in the liquid phase instantly, so the driving force is proportional to $1/R^3$ (R is the radius) which increases when temperature decreases, since the bubbles shrink; while the area of the bubble, which is proportional to R^2 , will decrease due to the shrinkage of the bubble. Considering the overall effect, the rate of mass transfer will increase under lower temperature, because it is proportional to $1/R$, which agrees with the result of the experiment.

By the end of 30 mins, the ozonolysis reaction for C18:2 and C18:3 under -78 °C was almost complete, while for C18:1 was about 95% converted. For the reaction conducted under 22 °C at the end of 30 mins, when conversion of C18:3 was almost 100%, C18:2 was about 95% complete and C18:1 was about 86%. The reaction rate for all the three unsaturated FAMES showed a decreasing order: C18:3 > C18:2 > C18:1. This result is consistent with that shown in Figure 3.1. This phenomenon may be explained by the difference of double bond number per molecule among different unsaturated esters, as the more double bonds present in the molecule, the more reactive the compound seems to be.

3.3.1.2 Continuous process

A continuous reaction was conducted in a vertical plug flow reactor embedded in a cooling jacket. The flow rate of feed (containing solvent and catalyst) varied from 3 to 27 ml/min. The pressure of input gas was around 21.5 psi with overall flow rate of 3.77 L/min and weight percentage of ozone of around 10.11%.

The yields of products under different flow rates are shown in Figure 3.3. Since the flow rate will affect the retention time of the materials, the yields of products under different flow rates varied significantly. With flow rate increasing from 3 to 15 ml/min, the yield of all the three aldehydes (hexanal, nonanal and methyl 9-oxononanoate) increased rapidly, almost twice of the starting value. However, a descending trend was observed for the aldehyde yields at flow rates higher than 15 ml/min. The change of yields for esters (methyl hexanoate, methyl nonanoate and dimethyl azelate) displayed a different feature compared to the change of aldehydes. Increase of flow rate resulted in a gradual decline of the yields for methyl esters, and when the flow rate approached a higher value (around 18 ml/min), the yields tended to be steady.

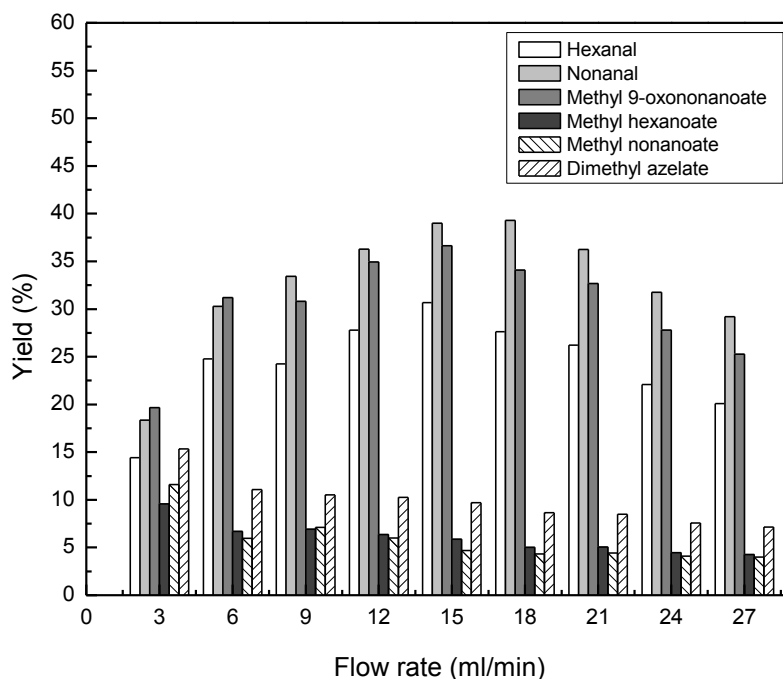


Figure 3.3 Molar yields of products from ozonolysis in methanol in plug flow reactor under different flow rates.

The total yields for parallel products obtained from the same reactants also showed a slight variation by increasing the flow rate of feed (Figure 3.4). Similar to the trend observed in Figure 3.3, the maximum product yields also appeared at a flow rate of 15 ml/min. However, when measuring the amount of individual unsaturated FAMES (Figure 3.5) and calculating their conversion profile as a function of feed flow rate, it is clear that at the flow rates between 3 and 12 ml/min, the reaction achieves maximum conversion (around 100% for most cases) and drops significantly for flow rates below 12 ml/min. This result is not consistent to the product formation profiles from Figure 3.3 and Figure 3.4, suggesting that at low liquid feed rates, where the ratio of ozone to FAMES is higher, reaction intermediates (e.g. ozonides) did not decompose to final product. From the GC analysis it was not possible to observe the formation of byproducts of FAME oxidation,

such as carboxylic acids, or ozonolysis intermediates in the methanol system. One hypothesis is that high ozone concentrations may stabilize ozonide intermediates, which are not detectable by GC, avoiding it to break into measurable product. However, additional work that is beyond the scope of this study should be performed to prove this hypothesis.

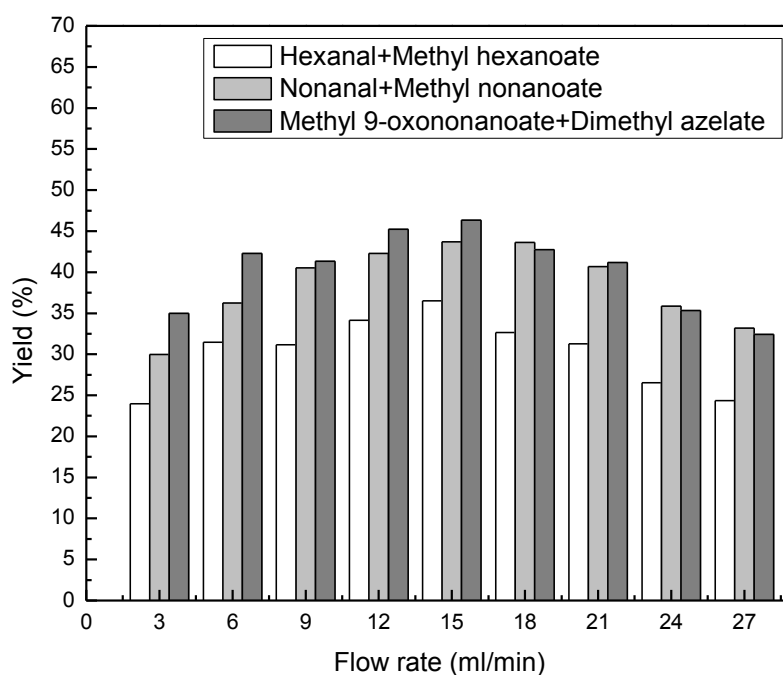


Figure 3.4 Total molar yields for products obtained from the same reactants from ozonolysis in methanol in plug flow reactor under different flow rates

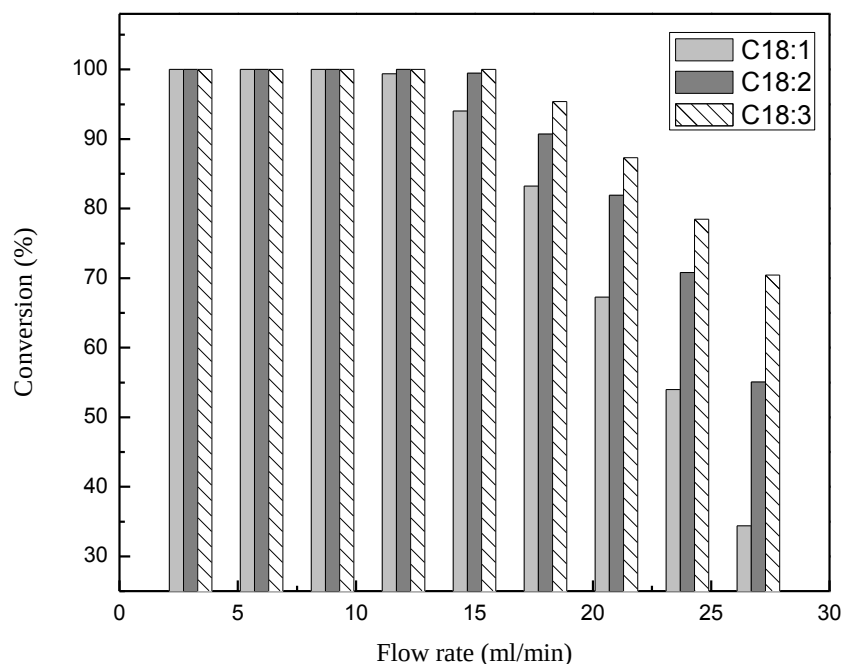


Figure 3.5 Conversion of unsaturated FAMES during ozonolysis in methanol in plug flow reactor under different flow rates

At the higher flow rates, the retention time for reaction is shorter and therefore, a decrease in conversion and on product formation was observed (Figure 3.4 and Figure 3.5). The aldehydes that are formed and some unreacted ozonides can be converted to esters by an extra conversion step with Oxone, as previously mentioned. However, to avoid extensive Oxone usage, it is important for the reaction system that we can achieve high product formation levels after the ozonolysis step. With the aim of optimizing the flow rate for maximizing both product formation and conversion of FAMES into aldehydes or esters, the flow rate of 15 ml/min is recommended for the methanol system.

3.3.2 Oxone treatment and extraction of ozonolysis products in methanol system

Further Oxone oxidation of the ozonolysis product mixture was conducted at room temperature (22 °C) under constant magnetic stirring at 500 rpm. Room temperature was chosen because the residual peroxides generated from ozonolysis are less reactive at low temperatures but high temperatures could also potentiate uncontrolled exothermal reactions and therefore, room temperature can help to accelerate their decomposition safely.

Two samples were prepared using product obtained from the continuous ozonolysis process, with the yields of 57% 9-oxononanoate and 18% dimethyl azelate. Oxone was added to the sample in two distinct loading processes: one-time batch load and a fed-batch load. In the first sample, 30 g of Oxone was added initially to 180 g of ozonolysis product, and the reaction was maintained for 19.30 hrs in total. During this period, 0.5 ml of sample was collected for GC analysis every 1-4 hrs without disturbing the reaction. For the fed-batch process, Oxone was added in 10 g aliquots every 5 hours for three times and analyzed in the same way as the first sample. After 15 hours, an extra 10 g of Oxone was added into sample under agitation for another 5 hrs, allowing the conversion to reach 85%. At the beginning of the 21st hr, the addition of same amount of Oxone boosted the conversion to 90%. With no further increase in conversion the reaction was in balance. The results are displayed in Figure 3.6. With the fed-batch loading, the conversion over time was almost linear, while for the batch loading, the rate of conversion decreased after 2 hrs of reaction time. After 15 hrs of reaction, the total amount of Oxone consumed by both of the two processes was the same (30 g), however, the conversion was notably different. The interrupted process showed a conversion of around 70 %, with a tendency

for further increase, while the uninterrupted process reached a conversion of 50% and the curve almost reached to a platform. This demonstrated that the more efficient loading technique for Oxone is fed-batch addition. The reason that this could happen may be because of the decomposition of Oxone, according to DuPont, the time for 50% of active oxygen in Oxone (3 wt% solution at 32 °C) to decompose is around 2.5 hrs under 7.0 pH value [86].

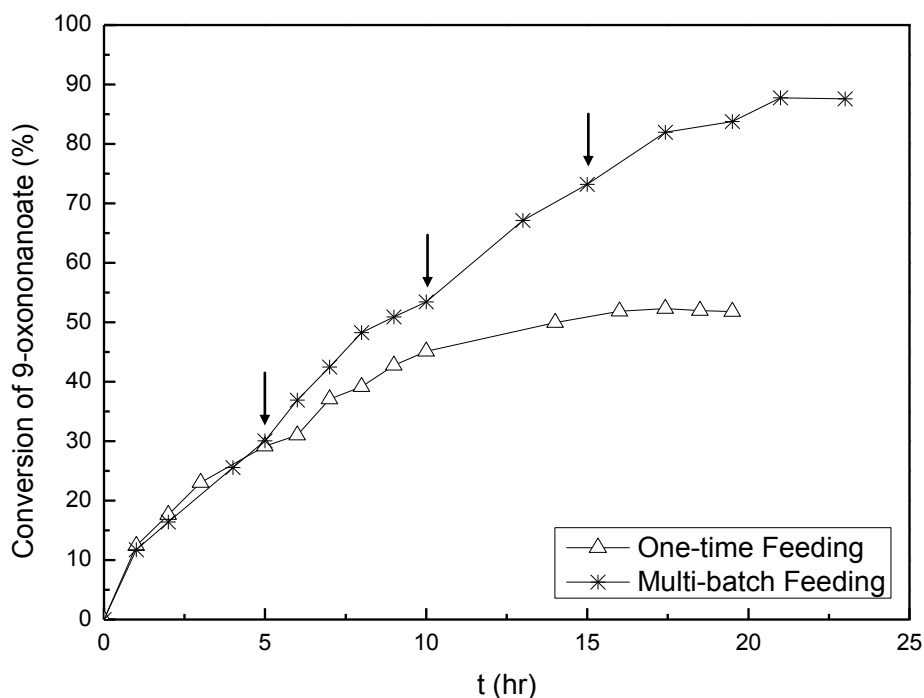


Figure 3.6 Kinetics for Oxone treatment of ozonolysis products

The GC analysis for products before and after Oxone treatment (using fed-batch load) is displayed in Figure 3.7. The result showed that most aldehydes were converted to methyl esters, with only trace amounts (less than 10% molar ratio) left in the final product solution. Peak G and H denote the two saturated FAMES which are methyl palmitate and methyl stearate. Since they do not react during the whole process, including ozonolysis

and Oxone treatment, they can be used as a reference to evaluate the overall yield for products.

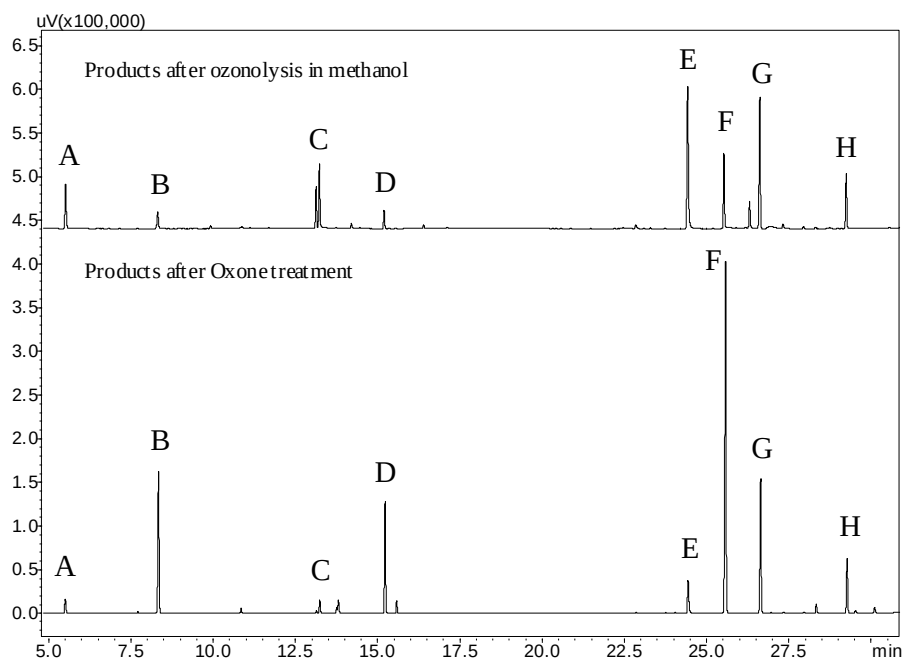


Figure 3.7 GC chromatograms for products before and after Oxone treatment. A: Hexanal; B: Methyl hexanal; C: Nonanal; D: Methyl nonanoate; E: Methyl 9-oxonanoate; F: Dimethyl azelate; G: Methyl palmitate; H: Methyl stearate.

After reacting the ozonolysis products with Oxone, an extraction step was required to separate Oxone reaction products from the dissolved salt. When using hexane as the extraction agent (Figure 3.8), the recovery for all of the organic material decreased steadily with the decreasing of ratio of hexane to sample solution. The best recovery observed among the 5 batches was 80% for dimethyl azelate and 90-100% for the other organic compounds except methanol, which was less than 20%. Compared with extraction by hexane, better results were obtained during water extraction (Figure 3.9). The recovery of the five methyl esters reached to a peak in batch 2, while the recovery of

methanol showed the highest value in batch 6. The best results, indicated in batch 2, showed recoveries of methyl hexanoate, methyl nonanoate, dimethyl azelate and methyl palmitate of around 90%. Only methyl stearate showed a slightly lower recovery (80%). Comparing both solvent systems for extraction of Oxone reaction products, water is preferred as it is more economical and safer to use in the industrial setup than hexane. The salt content was analyzed by drying a trace amount of material in an oven at 200 °C and taking the weight difference, the content dropped from 0.4% to 0.01%.

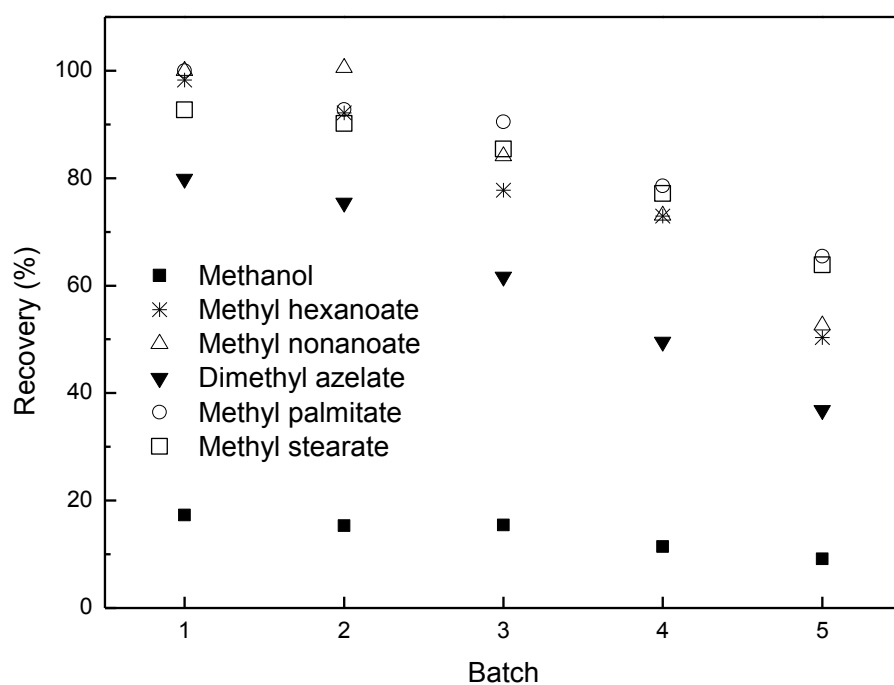


Figure 3.8 Extraction of products after Oxone treatment using hexane. From batch 1 to 5, the volumetric ratios of sample to extractant were 4:6, 4:4, 4:3, 4:2 and 4:1.

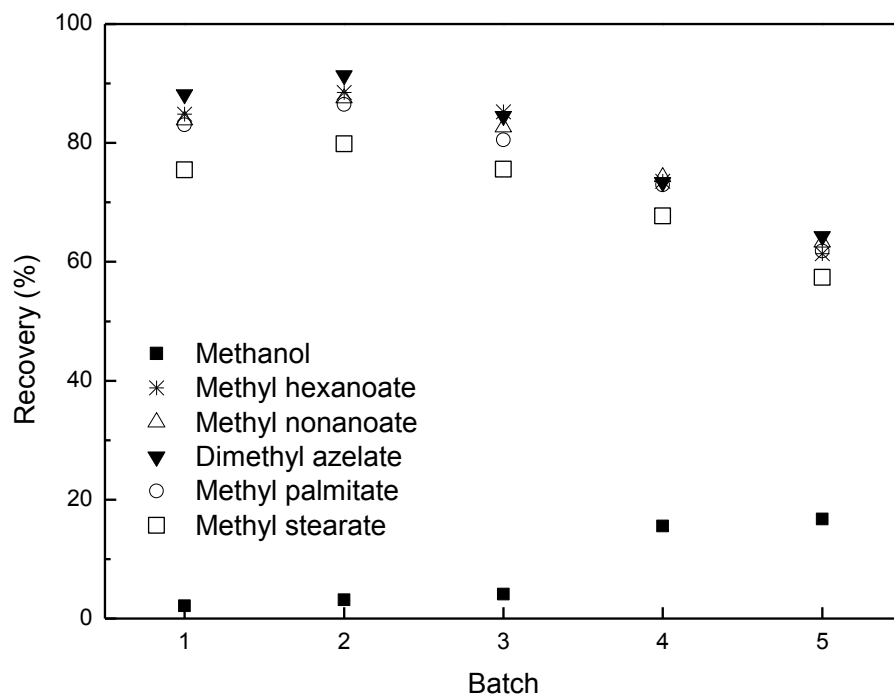


Figure 3.9 Extraction of products after Oxone treatment using water. From batch 1 to 5, the volumetric ratios of sample to extractant were 4:6, 4:4, 4:3, 4:2 and 4:1.

3.3.3 Mass transfer study of ozone in methanol system

In methanol system, the pure solvent was passed through the reactor with flow rate varied from 10 ml/min to 40 ml/min, and the conditions of gas phase are described in Figure 3.10. The concentration of ozone in methanol was measured in the reactor outlet as a function of solvent flow rate. As demonstrated in the figure, the concentration of ozone decreased significantly with increase of flow rate. This result suggests that the higher flow rate of solvent will reduce the contact time between the liquid and gas phases, thus the absorption of ozone into the liquid phase was lower. The duplicates of each experiment did not show good consistency, perhaps due to the fact that the sample

needed to be diluted 25 times before each measurement (to keep the absorbance between 0.0 and 1.0), where some operating errors may be introduced.

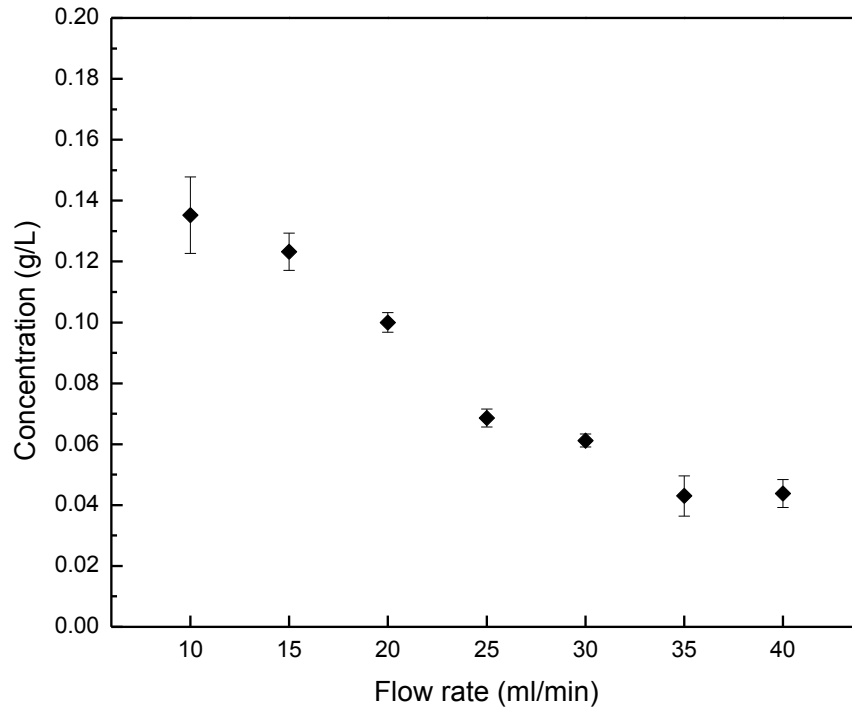


Figure 3.10 Concentration of ozone in methanol under different solvent flow rate at 22 °C with total gas pressure 20.89 psi, flow rate 3.75 L/min and ozone mass fraction 10.95%.

The value NTU of reactor calculated based on Equation 3.3 under different flow rates falls between 0.0011 and 0.002 without significant variation, as shown in Figure 3.11. This observation indicates that the gas phase NTU remains constant, at certain temperature, for the same absorption liquid in the experimental flow rate range (10-40 ml/min).

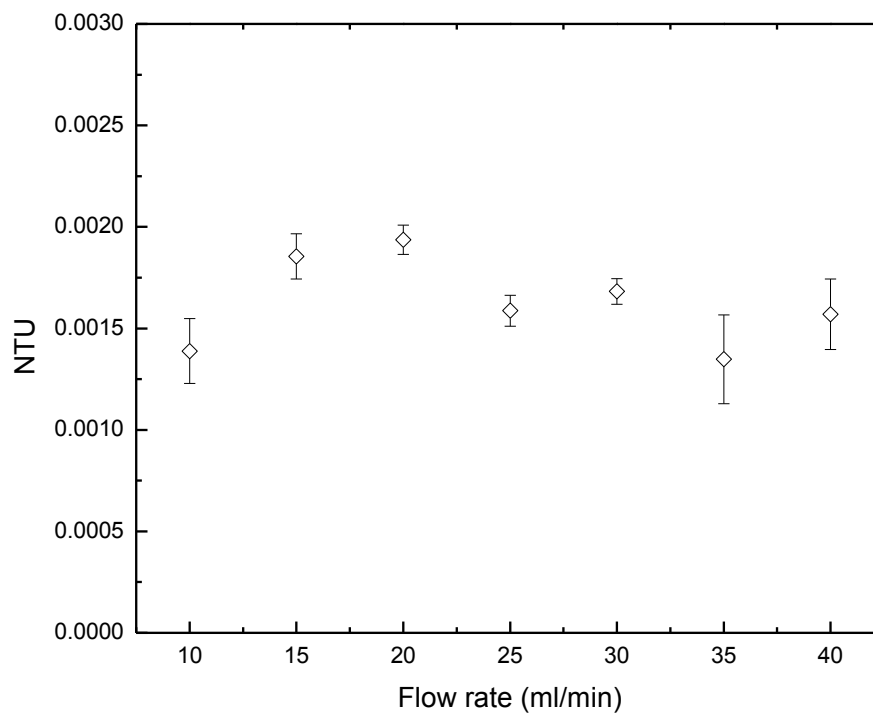


Figure 3.11 Gas phase NTU for ozone in methanol for PFR reactor under different solvent flow rate at 22 °C with total gas pressure 20.89 psi, flow rate 3.75 L/min and ozone mass fraction 10.95%.

Considering the entire sample results for the different liquid flow rates, a box plot was applied and the result is shown in Figure 3.12. The mean value and median value of NTU for ozone mass transfer in methanol are both around 0.0015.

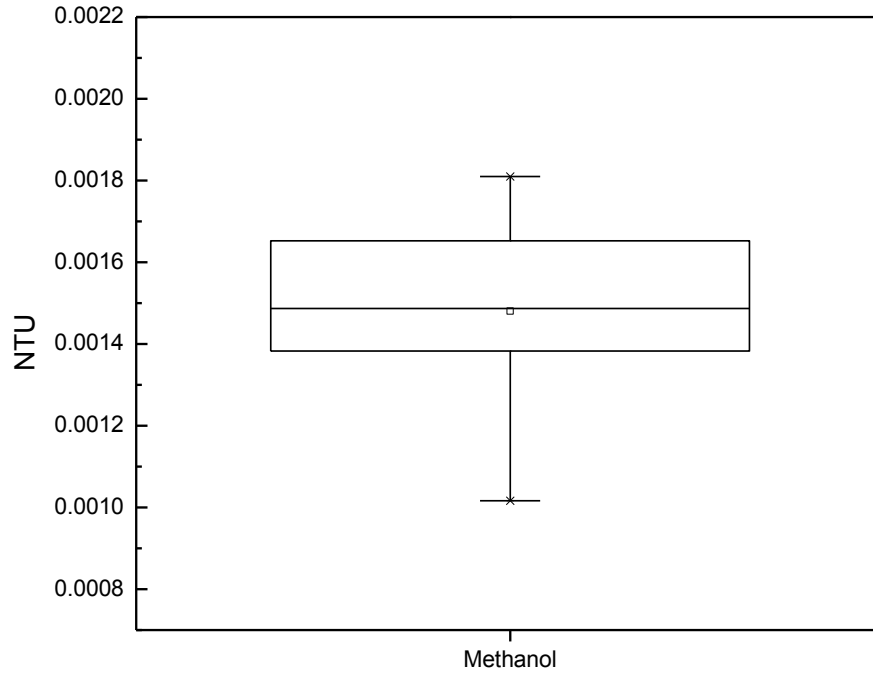


Figure 3.12 Box plot of gas phase NTU for ozone mass transfer in methanol in PFR reactor under different solvent flow rate at 22 °C with total gas pressure 20.89 psi, flow rate 3.75 L/min and ozone mass fraction 10.95%.

Using the median value of 0.00148 for gas phase NTU, the gas phase HTU was calculated as 74.07 meters using Equation 3.2. Applying Equation 3.7 and Equation 3.8, the resulting mass transfer coefficient $K_x a$ was 0.138 mol/m³s.

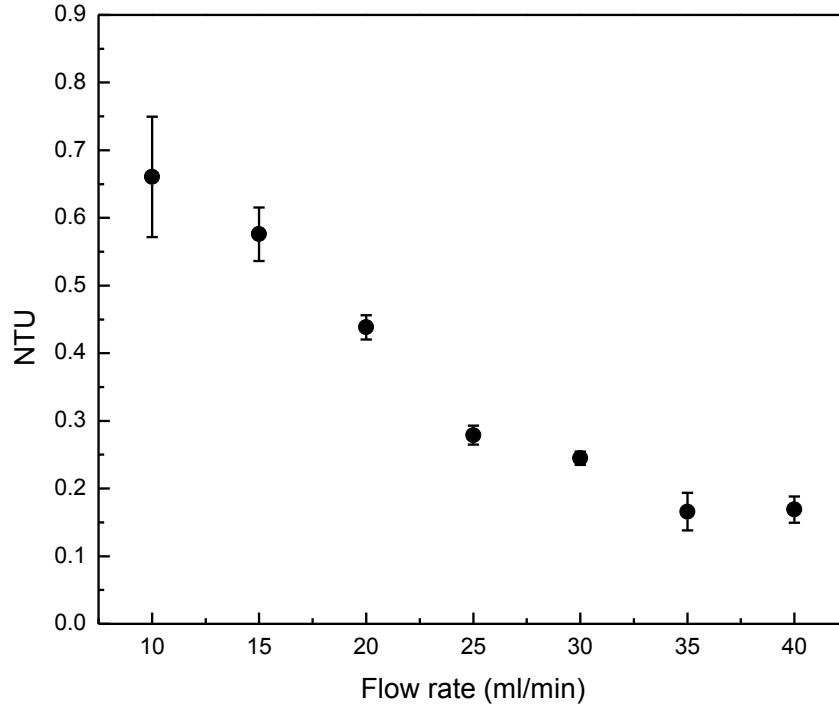


Figure 3.13 Liquid phase NTU for ozone in methanol in PFR reactor under different solvent flow rate at 22 °C with total gas pressure 20.89 psi, flow rate 3.75 L/min and ozone mass fraction 10.95%.

The NTU under different flow rates of methanol in liquid phase was also calculated using concentration data from Figure 3.10. Unlike in the gas phase, the value of NTU drops from 3.66 to 1.7 with flow rate increasing from 10 to 40 ml/min as indicated in Figure 3.13. This result shows that the mass transfer efficiency in the liquid phase is affected more significantly by the speed of liquid flow. Applying Equation 3.2 and using the average value of NTU from Figure 3.13, the liquid phase HTU was calculated as 0.34 m. By inputting this number into Equation 3.9 and Equation 3.10, the corresponding mass transfer coefficient $K_x a$ was obtained as 21.313 mol/m³s. Since the calculated mass transfer coefficient in the gas phase is much lower than that in the liquid phase, we use

the gas-phase value as the approximate overall mass transfer coefficient to simplify the process.

3.3.4 Ozone mass transfer in water system

Mass transfer in the same PFR reactor using water as solvent was also evaluated under the same condition as using methanol. Water was fed into reactor with flow rate changing from 10 ml/min to 60 ml/min and the concentration of ozone in outlet liquid phase was measured under each flow rate. Unlike the result shown above for methanol system, the concentration of ozone in solvent did not change significantly with the increase of water flow rate. This happened was because the water solution was already saturated by ozone under the experiment condition: ozone partial pressure was around 1.58 psi, and according to Henry's law and the known Henry's law constant of 85922.55 psi/(mol fraction), the equilibrium concentration of ozone should be 0.049 g/L, which is highly consistent with result shown in Figure 3.14.

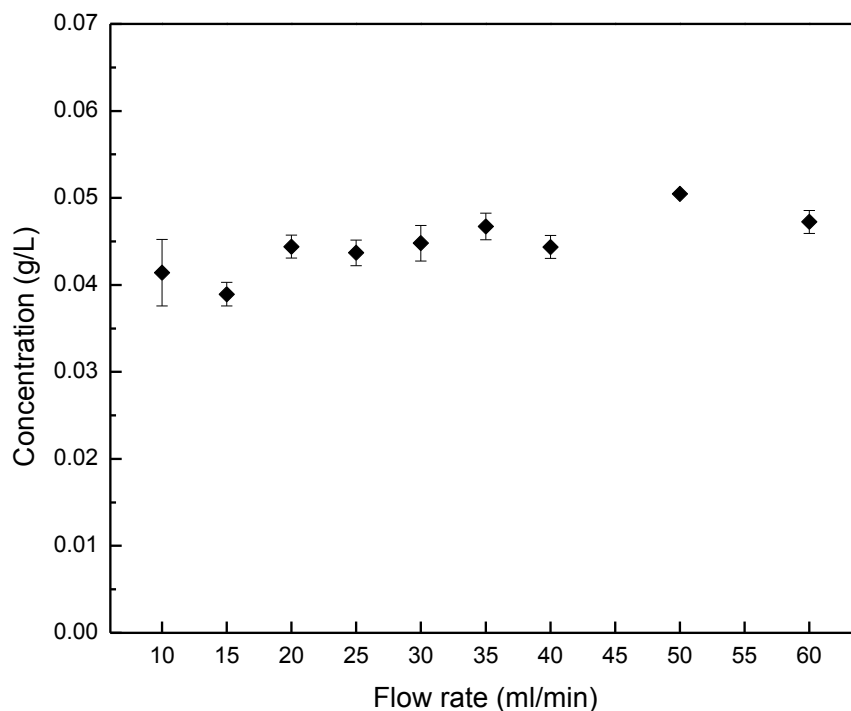


Figure 3.14 Concentration of ozone in water with different solvent flow rate at 22 °C with total gas pressure 20.89 psi, flow rate 3.75 L/min and ozone mass fraction 10.95%.

Since the solution was saturated with ozone for almost all the flow rate conditions, the NTU calculated for corresponding flow rate is now dependent on the flow rate, and the NTU value in this circumstance is not accurate anymore, thus, it is not possible to continue the study for mass transfer calculation in water system.

3.3.5 Ozone mass transfer under reaction in methanol system

According to the previous study, the mass transfer of ozone between gas phase and liquid phase will be enhanced by the reaction [77], and this enhancement factor “E” is defined as the actual rate of mass transfer with ozone reactions divided by the maximum rate of physical absorption without any reaction. In this section, we will calculate the enhancement factor for ozonolysis of FAMES in methanol.

As observed from Figure 3.2, the reaction rate of ozonolysis is controlled by ozone mass transfer between gas and liquid phase in methanol system. Therefore, we used the data for conversion of unsaturated FAMES during ozonolysis from Figure 3.5 and calculated the ozone required under different flow rates based on stoichiometry. Because the reaction is mass transfer driven, we assume that if the conversion is not 100%, it is because the ozone obtained from the liquid already reaches to the limit amount. Based on this assumption we obtained the actual rate of ozone mass transfer for flow rates under which conversions of FAMES were less than 100%. As shown in Figure 3.15, these flow rates are from 15 to 27 ml/min. It is also displayed that the rates of mass transfer actually reached to maximum value with flow rate of 15 ml/min or higher.

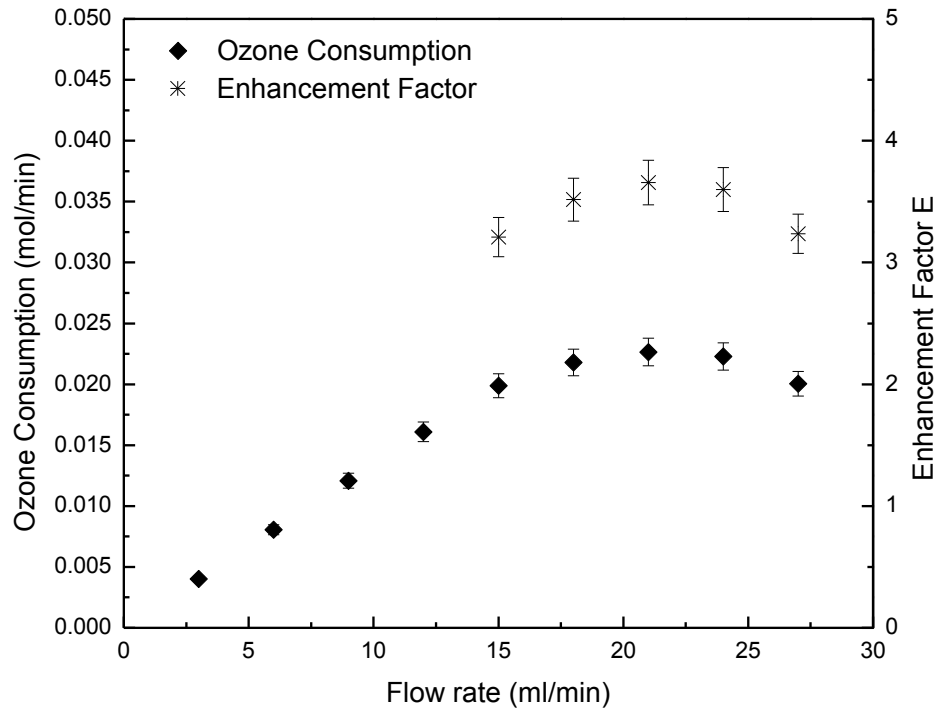


Figure 3.15 Ozone consumption and enhancement factor for ozone mass transfer with ozonolysis in methanol in PFR reactor under different material flow rate at 22 °C with total gas pressure 21.5 psi, flow rate 3.77 L/min and ozone mass fraction 10.11%.

The rates of mass transfer for ozone without any reaction was calculated using Equation 3.11, where y^* was assumed 0, because with presence of ozone reaction, ozone in liquid phase is assumed to be consumed instantly due to the high reaction rate compared to mass transfer rate. Also we assumed the value of $K_y a$ was constant, because the temperature change during reaction was not very high – the input gas phase temperature was around 32 °C and the input and output temperatures of liquid phase was 22 °C and 33-36 °C, respectively. The enhancement factor values were calculated by applying the definition, as shown in Figure 3.15 with an average value of 3.44. This value is

comparable to the result reported by Zhou, et al. [67] , which was between 1 and 9 under different ozone reactions in water.

3.3.6 Reaction kinetics of ozonolysis in water system

3.3.6.1 Batch process

Ozonolysis in water system was carried out in the same experimental setup as in the methanol system described above. The batches of 20 g of FAMEs were diluted in 60 g of distilled water without adding any catalyst. Before the reaction, materials were left in the ice bath for 1 hour to be cooled down to near 0 °C. After the reaction started, the temperature increased steadily from 2 °C to more than 50 °C (Figure 3.16) and this trend lasted for 39 mins. When the temperature stopped increasing, it indicated that the reaction was complete. As a contrast, the pH value of the mixture was decreasing during the process and at the end of the reaction, the pH value reached to about 2 (Figure 3.17). The temperature change shows that ozone reaction is exothermal and needs to be applied with cooling system to control the temperature in a lower range. The decrease of pH value should be caused by the generation of acids that are slightly soluble in water.

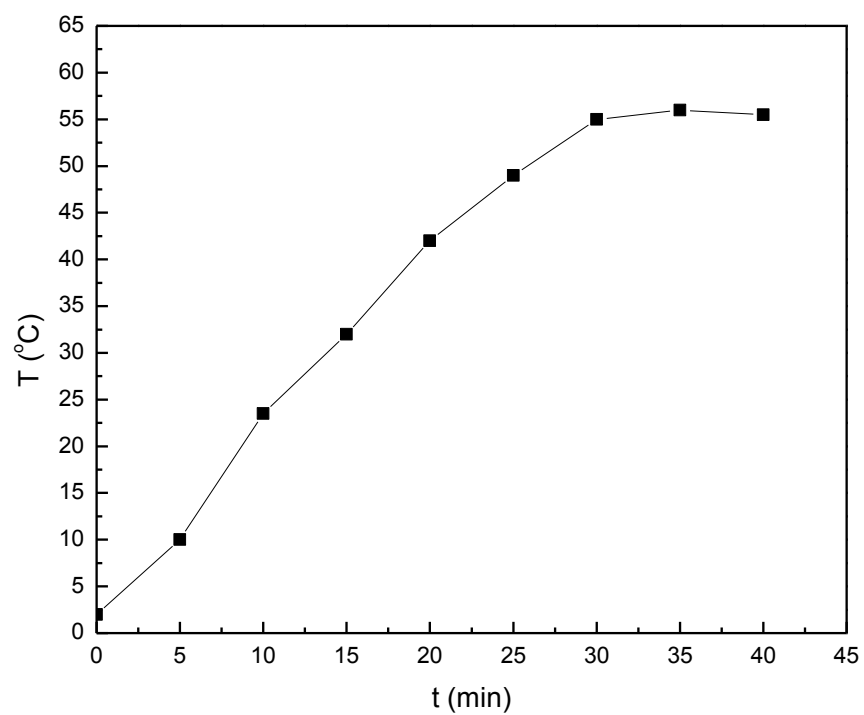


Figure 3.16 Temperature of solution during ozonolysis reaction

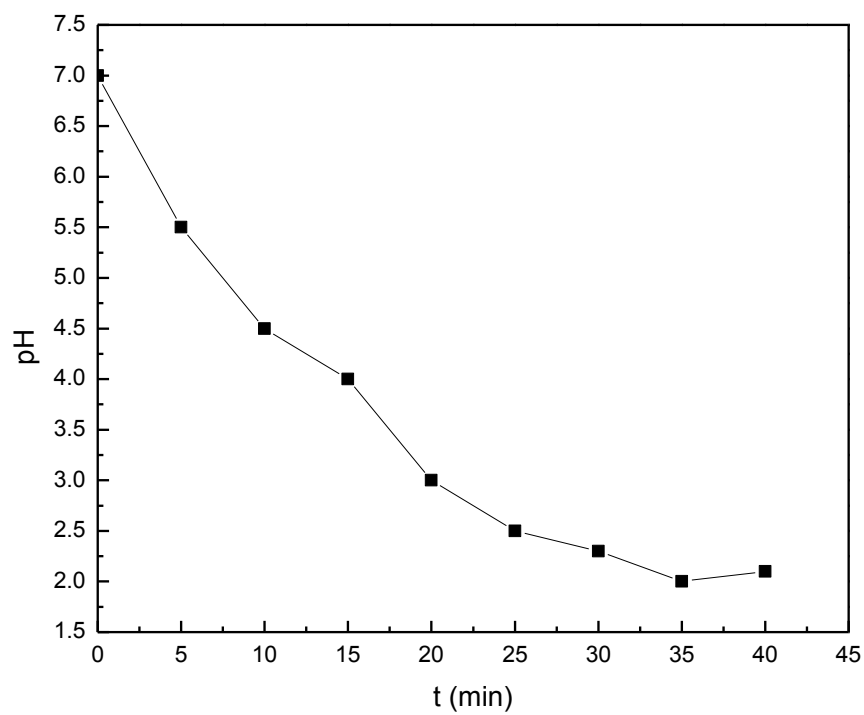


Figure 3.17 pH change of water phase during reaction

Figure 3.18 shows the comparison between kinetics for ozonolysis in water and methanol system. Under the same flow rate of reactant solution, gas pressure and mass concentration of ozone, the reaction for all three unsaturated FAMES in water was finished in 45 mins, while reaction in methanol proceeded slightly faster (about 5 mins) than that in water. The reason for this observation could be that the reaction in water is occurring between three phases, rather than two phases as in methanol, which exerts more resistance to mass transfer. Similar to the methanol system ozonolysis kinetics, the higher rate of conversion was also observed for FAMES containing more double bonds (e. g. C18:3 > C18:2 > C18:1).

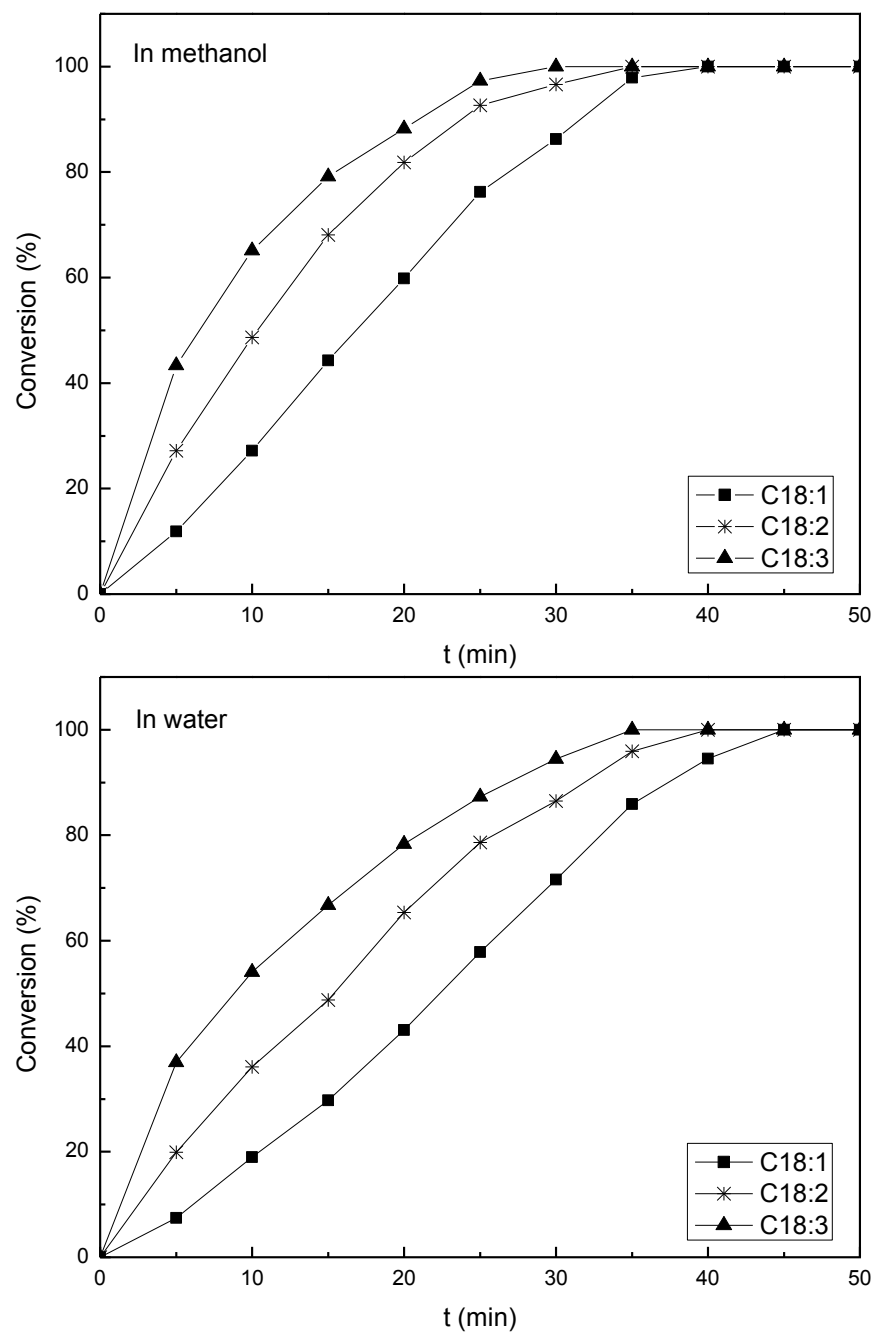


Figure 3.18 Ozonolysis of FAMES in two solvent systems at room temperature

3.3.6.2 Continuous process

In the continuous reaction mode, FAMES and water with a mass ratio of 1:3 were added to a conical flask and mixed under high speed agitation. A peristaltic pump was used to supply the material into the reactor at constant flow rate. The flask stored with material was connected to the reactor through a tube containing a static mixer, which can keep the material emulsified. The pressure of input gas was around 21.7 psi at a flow rate of 4.72 L/min with the weight percentage of ozone around 11.07%. Cooling water was applied to keep the reactor as well as the ozonator under lower temperature. The only variable was the material flow rate, which was changed from 20 L/min to 50 L/min while conducting different batches of experiments. The purpose of this experiment was to examine the effect of material flow rate on the yield and profile of products, so that an optimal flow rate can be recommended.

Figure 3.19 displays the conversions of 3 unsaturated FAMES obtained under different flow rates. The products formed under flow rate equal or lower than 30 ml/min showed 100% conversions of FAMES, while under 50 ml/min the conversions dropped significantly, especially for C18:1 and C18:2. The reactor volume is 0.75 L, so the retention times for each flow rate from 20 ml/min to 50 ml/min are 37.5, 25, 18.75 and 15 min, the stoichiometric flow rates of ozone for each material flow rate are 2.34, 3.51, 4.67 and 4.69 L/min with the same gas pressure and ozone mass fraction as described above.

The specific yields for all the products are displayed in Figure 3.20. From these results we can see that the production of acids consistently decrease as the flow rate increases,

while aldehydes show a peak of yield at 40 ml/min, similarly to what was observed for the methanol system.

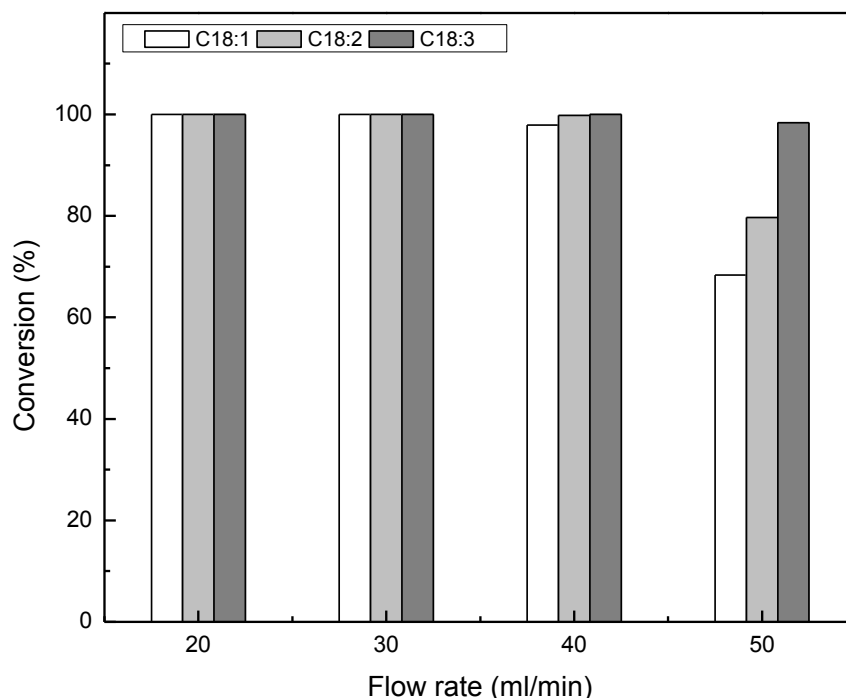


Figure 3.19 Conversions of unsaturated FAMES at different material flow rate for ozonolysis in water in continuous reactor.

The overall molar yields of products, including both aldehydes and acids contributed by the same unsaturated FAMES are plotted in Figure 3.21. Unlike the yield profiles for aldehydes in Figure 3.20, the peak for overall yield of methyl 9-oxononanoate and monomethyl azelate was obtained at 30 ml/min, for nonanal and nonanoic acid shows at 20 ml/min, and for hexanal and hexanoic acid the difference is not obvious between flow rate of 20 ml/min and 30 ml/min. This can be explained as follows: under flow rate that is higher than 40 ml/min the reactants were not completely consumed (as shown in Figure 3.19), so the increase of flow rate will cause the increase of overall product yields; once the flow rate is lower than 40 ml/min, since the conversion of FAMES was 100% or very

close to it, more reaction time will cause the generation of more acids from aldehydes, which results in a decrease of aldehydes and increase of acids. Since the target products for this reaction were aldehydes, from Figure 3.20 we can conclude that the optimal material flow rate is around 40 ml/min.

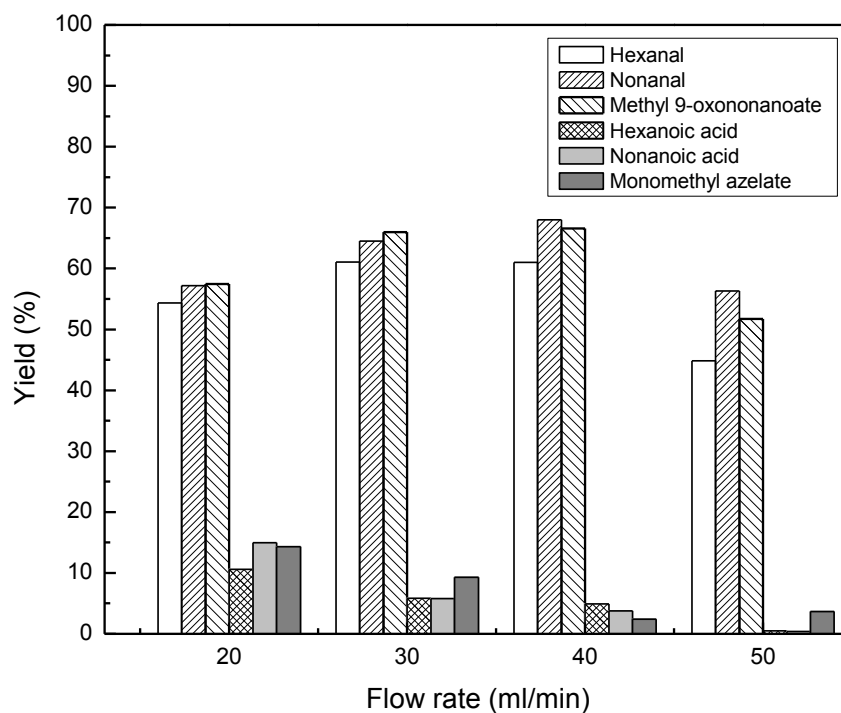


Figure 3.20 Product yields at different material flow rate for ozonolysis in water in continuous reactor.

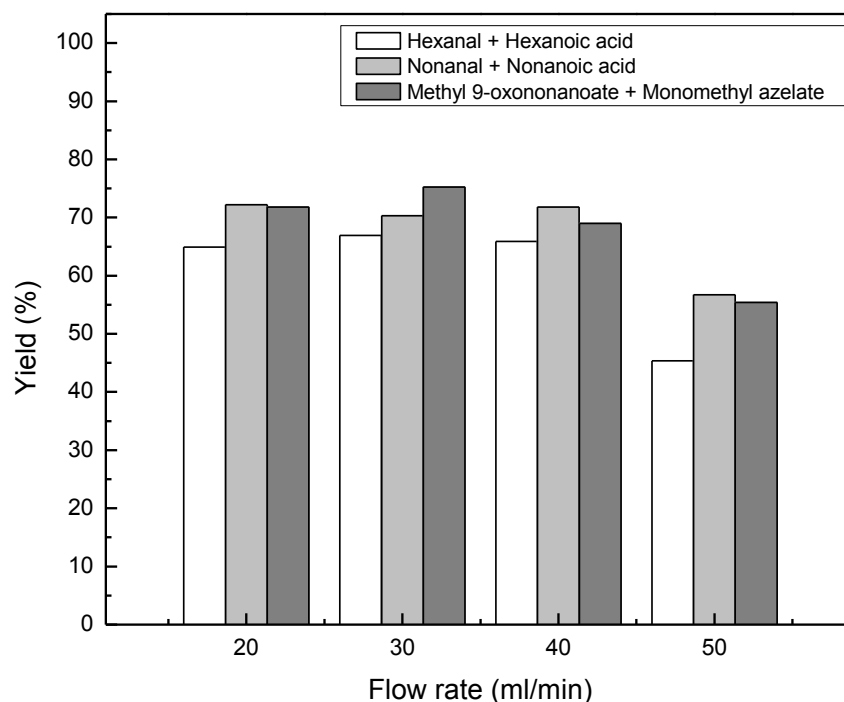


Figure 3.21 Total molar yields for products obtained from the same reactants from ozonolysis in water in plug flow reactor under different flow rates.

3.4 Conclusion

Ozonation of FAMEs produced from Soybean oil using methanol as solvent and sodium methoxide as catalyst was carried out in both semi-batch and continuous processes to study reaction kinetics. Using dry-ice-acetone cooling system to control the temperature at -78°C showed to be the best method to achieve the highest conversion rates, however, the reaction rate difference among different temperatures was not highly significant. The optimal flow rate for the continuous process was suggested to be around 15 ml/min, where the production of esters and aldehydes were maximized. The kinetics also indicated that the most unsaturated ester (C18:3) had the highest reaction rate, followed by C18:2 and C18:1, which can be explained by the highest number of double bonds per FAME molecule. Complete unsaturated FAMEs conversion was obtained for liquid flow

rates between 3 and 15 ml/min, decreasing significantly for flow rates higher than 15 ml/min. This observation and the fact that aldehyde and ester yields peaked at 15 ml/min in the continuous reaction, suggests that the higher concentrations of ozone, which are obtained at lower FAME solution flow rates, may promote the stabilization of reaction intermediates that cannot be detected using GC methodology and could not be quantified. Further studies beyond the scope of this work should address this topic to understand the effect of ozone concentration in the inhibition of aldehyde and ester formation during ozonolysis in solvents like methanol.

As the target products from ozonolysis in methanol are methyl esters, the oxidation from aldehydes to esters was accomplished by Oxone treatment. A best conversion of 88% for 9-oxononanoate, was reached according to the experiment results and the total yield of dimethyl azelate was 68%. In order to remove the salt residues from the product solution, extraction using both hexane and water was conducted. Based on the comparison of recovery of organic compounds water performed better than hexane.

Mass transfer of ozone in pure methanol was studied by applying the number of transfer units (NTU) theory, which is a simplified model for studying gas-liquid mass transfer. It was found that the NTU value for the gas phase of ozone mass transfer in methanol is around 0.0015. Also, the combined mass transfer coefficient $K_y a$ for gas phase calculated based on NTU value for methanol system is $0.0087 \text{ mol/m}^3\text{s}$.

Ozonolysis of FAMES in water without catalyst was also conducted in both semi-batch reactor and continuous reactor. It was found that the reaction was highly exothermal,

generating increase in reaction temperature even under cooling conditions, and formed acids that caused the pH value to decrease during the course of reaction.

The conversion rate of FAMEs during ozonolysis in water and in methanol was also compared. The results show that the conversion rate is slightly higher in the methanol system than in water. The observed difference may be due to the fact that in water system there are three phases present while in methanol, the reaction takes place in two phases.

The optimal material flow rate in continuous reaction for the water solvent system was found to be around 40 ml/min, given a constant ozone gas input 21.5 psi at a flow rate of 4.72 L/min with the weight percentage of ozone around 11.07%. Higher flow rate will cause incomplete conversion of reactants and lower flow rate will generate higher molar yield of acids and therefore reduce the aldehydes yield.

Chapter 4: Distillation Process Design to Separate Ozonolysis Products of FAMES

4.1 Introduction

During last chapter we discussed the reaction kinetics in methanol system and water system. Multiple products were formed from the reactions including aldehydes and methyl esters. In addition to the newly formed compounds, the two saturated methyl esters (methyl palmitate and methyl stearate) also remained in the systems; therefore, the compositions of the product solutions are quite complex. The project objective is to develop and produce biobased polymer building blocks which would be dimethyl azelate from the methanol system and the aldehydes (hexanal and nonanal) from water system, probably also methyl 9-oxononanoate from both systems depending on the performance of the derived polymer from this compound. According to the polymer theory, high purity of monomers increase the degree of polymerization and thus provides higher molecular weight and often better polymer properties. Therefore, purification of the products is very important for polymer application. Besides, even for the other output chemicals that will not be used to produce biobased polymers, such as methyl hexanoate and methyl nonanoate, a higher purity will always increase the marketing value of the products.

Distillation is the most widely used technology in the chemical industry to separate and purify chemicals. Fractional distillation was developed by Tadeo Alderotti in the 13th century [87], and since then, the simulation study on distillation became increasingly efficient. One of the most powerful software used by engineers to conduct distillation simulation is Aspen Plus.

Aspen Plus is a chemical process optimization software created in the 1980's and has been used by the chemical, biochemical and polymer industries to simulate their processes. It supports design, operation, and optimization for both manufacturing and separation processes. It also contains batch simulation, dynamic simulation and economic evaluations [88].

Aspen Plus is a very powerful software, given proper input values and assumptions, it can provide very accurate results. In order to properly develop a simulation for distillation process, there are several factors that should be taken into consideration. The first and most important factor is the physical properties of the components of the mixture, such as VLE data and enthalpy of evaporation of components. Most data for the properties of compounds related to this project is reliably provided in the modern version of Aspen. However, for some components that are not included in ASPEN database (e.g. 9-oxo-nonanoate), thermodynamic properties can be estimated using group contribution method by UNIFAC functional groups in the data properties module of Aspen Plus. Parameters estimated by Aspen include: 1) ideal gas heat capacity coefficients; 2) Antoine liquid vapor pressure coefficient; 3) DIPPR liquid heat capacity coefficients; 4) Watson heat of vaporization parameters; 5) DIPPR liquid thermal conductivity coefficients; 6) Andrade liquid viscosity coefficients; 7) DIPPR vapor viscosity coefficients; 8) DIPPR surface tension coefficients.

Another concern before starting the distillation design is the separation sequence. In this project the sequence was determined by the heuristic method. In this method, the volatility, corrosivity and reactivity were fully considered to assign different priorities to components. Separation order is important because it can significantly impact on the

separation cost especially in terms of energy cost. For example, in an improper design, some components would be repeatedly heated up and cooled down before leaving the system.

The third consideration in distillation modeling is to decide operating pressure and temperature. The pressure of distillation column is normally determined based on the temperature of cooling medium at the reflux condenser. Generally, it is desirable to operate the column at as low a pressure as possible, to maximize the relative volatility, this is to facilitate the better separation, because the relative volatility goes on increasing as we reduce the separation pressure. The two factors pressure and temperature are highly correlated and should be determined also based on equipment cost considerations. Stability of products should also be evaluated, for instance, some components may decompose or get oxidized under higher temperature. In this case, the cost of energy or equipment should be given secondary importance.

In this chapter we addressed all the issues mentioned above and eventually proposed the distillation design for products generated through ozonolysis in both methanol and water system, as described in chapter 3. The dimensions of equipments and operation conditions will also be specified based on the simulation results.

4.2 Heuristic method to determine distillation sequence [89]

- a. If there are only two products in a mixture and all of the components in one product are more volatile than all of the components in the other product, then separate the components into two products first;
- b. If a component is corrosive, unstable, reactive or otherwise hazardous, then remove this component from bulk stream first;

- c. If the most volatile component in the mixture is $>\sim 20$ mol% of the feed, and it has the largest mole fraction in the feed, the second-largest-mole-fraction component is less than 90% of the most volatile component, and the proposed separation is one of the easiest separations remaining, then split off the most volatile component as distillate;
- d. If the least volatile component in the mixture is $>\sim 20$ mol% of the feed, and it has the largest mole fraction in the feed, the second-largest-mole-fraction component is less than 90% of the most volatile component, and the proposed separation is one of the easiest separations remaining, then split off the least volatile component as bottom;
- e. If a separation has a distillate-to-bottom molar ratio of $\sim 40:60$ to $60:40$ and the proposed separation is one of the easiest separations remaining, then the next separation should be the one closest to 50:50 distillate-to-bottom ratio;
- f. If none of the above apply, then the next separation to be done should be the easiest, i.e. the one with the highest separation coefficient, S , defined as $S = (\alpha - 1) * (D/B)$ for $D/B < 1$, and $S = (\alpha - 1) * (B/D)$ for $D/B > 1$, where α is the ratio of relative volatility of adjacent components, D is the molar flow rate of the distillate, B is the molar flow rate of the bottoms.

4.3 Distillation sequence for ozonolysis products

Products prepared from ozonolysis in methanol after being dried using molecular sieves contain 6 main components with a little amount of unknown impurities ($< 0.3\%$ mass ratio). To simplify the design, the portion of unknown compounds was added as methyl palmitate and methyl stearate, with the assumption that they are mainly heavy

compounds. As shown in Table 4.1 (products were prepared by continuous ozonolysis reaction in methanol, with gas flow rate of 3.75 L/min containing 10.91 wt% ozone, and liquid reactants flow rate of 12 ml/min; FAMES to methanol mass ratio was 1:2), the most abundant compound is methanol, which takes up 83.96% of molar ratio in the total mixture. The second most abundant compound is dimethyl azelate, which has a molar ratio of 7.46%, and this is also the most important product. All the other compounds are relatively low in molar quantity.

Table 4.1 Products generated from ozonolysis in methanol after Oxone treatment and water extraction

Index	Component	mol%
1	Methanol	83.96
2	Methyl hexanoate	5.04
3	Methyl nonanoate	2.11
4	Dimethyl azelate	7.46
5	Methyl palmitate	1.06
6	Methyl stearate	0.4

Examining the heuristic rules in 4.2, a and b do not apply, since we have more than two products to purify; according to c, methanol should be separated first. After methanol is separated from the mixture, the composition and volatilities for each compound are given below in Table 4.2. The remaining three products that are of interest are methyl hexanoate, methyl nonanoate and dimethyl azelate. Rule c and d also do not apply,

because neither methyl hexanoate nor methyl stearate has the largest mole fraction, whereas dimethyl azelate has.

The next rule e is the one we should follow. The reason is if we split methyl hexanoate and methyl nonanoate as the distillate stream, and the remaining compounds as the bottom stream, the molar ratio between the two mixtures is 44.5:55.5 which is quite close to 50:50. Thus, these two methyl esters were chosen to be distilled first as a mixture, and then separated in the next column. Dimethyl azelate will be separated from the heavy compounds in the consequential process, using another parallel column. The overall process diagram will be displayed in the design section.

Table 4.2 Molar ratio of compounds after removing water and methanol

Product	Component	Concentration mol%	Bp, at 0.3 atm. °C	Adjacent relative volatility	Separation coefficient
1	Methyl hexanoate	31.36	113	7.91	1.9603466
2	Methyl nonanoate	13.13	169	16.9	7.55132743
3	Dimethyl azelate	46.42	171 (0.04 atm)	6.69	2.43857143
4	Methyl palmitate	6.60	211 (0.04 atm)		
	Methyl stearate	2.49	234 (0.04 atm)		

The distillation sequence for the second set of products (all the products in Table 4.2) can also be determined similarly. These products were made by applying ozonolysis in water and then were dried for 24 hrs using molecular sieves (3 A beads purchased from Sigma-Aldrich) after reaction. This mixture consists of five compounds, which are listed in Table 4.3 with the corresponding molar fractions for each component. The most abundant

compound in this mixture is methyl 9-oxononanoate, which takes up more than 46% in molar ratio. The second most abundant product in this mixture is hexanal, with molar ratio of 28.48% followed by nonanal with 13.32%. Saturated esters including methyl palmitate and methyl stearate will be separated as a mixture product.

Table 4.3 Products generated from ozonolysis in water

Index	Component	mol%
1	Hexanal	28.48
2	Nonanal	13.32
3	Methyl 9-oxononanoate	46.42
4	Methyl palmitate	8.75
5	Methyl stearate	3.02

Compounds in this mixture have similar structures and compositions compared to products from ozonolysis in methanol, therefore a similar separation order should be implemented. In this case, rule a, b, c, d do not apply, and according to rule e, hexanal and nonanal will be separated together as distillate in first the column, with the other compounds coming from bottom. This split gives a molar ratio of 41.8:51.2, which is also close to 50:50. Because no solvent needs to be removed in the water system, this distillation process consists of three columns.

4.4 Properties for main components

Properties for the main products prepared by ozonolysis using methanol and water systems are displayed in Table 4.4. Most of the properties were obtained from Aspen Plus

databank, however for some compounds that could not be found in the databank, online resources and literature was used. According to the boiling point data, separation for methyl 9-oxononanoate and dimethyl azelate requires high temperature and therefore, in order to prevent the products from decomposing, vacuum distillation would be applied. Among all the properties, vapor pressure and heat of evaporation are the most important data for distillation simulation, because in distillation design, all the calculations are based on these data, and if they are not accurate, the consequential design could be very unrealistic. For all the ozonolysis products, the compounds that cannot be found in the databank are methyl 9-oxononanoate and dimethyl azelate. The properties for this compound were estimated by Aspen Properties. For this purpose, the chemical structure and functional groups were added to the software for group contribution method and UNIFAC functional groups were applied. Property estimation can also be conducted using regression method, if experimental data of thermodynamic properties for these compounds is available from literature. However, no data was found for methyl 9-oxononanoate and dimethyl azelate and therefore, the estimation only relied on theory.

Table 4.4 Properties for main products from ozonolysis

Properties	Formula	Molar weight	Density	Molar volume	Boiling point	Heat of evap.	Vapor Pressure	Viscosity
Signs	---	Mw	ρ_i	V_i	Tb	ΔH_i	P_0^*	v_i
Units	---	g/mol	kg/m ³ (at 25 °C)	10 ⁻³ m ³ /mol	°C	kJ/mol	kPa (at 25 °C)	cP(mPa·s)
Water	H ₂ O	18.02	1000	0.018	100	39.5 ⁿ	3.17	0.89 (25 °C)
Methanol	CH ₄ O	32.04	791.8	0.0405	65	35.28 ^g	13.02	0.521 (30 °C) ⁿ
Hexanal	C ₆ H ₁₂ O	100.161	833.5	0.1237	131	31.65	1.51	0.69(20 °C)
Nonanal	C ₉ H ₁₈ O	142.24	826.4	0.1744	191	43.49	0.0493	---
Methyl Hexanoate	C ₇ H ₁₄ O ₂	130.185	884.6	0.1472	151	48.7	0.072	0.525 (25 °C) ⁿ
Methyl Nonanoate	C ₁₀ H ₂₀ O ₂	172.268	875 ^a	0.1969	213.5 ^c	63.2 ^h	0.0257	0.68 (25 °C) ⁿ
Methyl 9-oxononanoate	C ₁₀ H ₁₈ O ₃	186.248	958	0.1944	249.4 ^d	48.66 ^d	3.07E-03 ^d	---
Dimethyl Azelate	C ₁₁ H ₂₀ O ₄	216.27	1007	0.2148	294.4 ^e	51.45 ^e	6.55E-04	---
Methyl Palmitate	C ₁₇ H ₃₄ O ₂	270.46	852	0.3174	417 ⁿ	62.42 ⁿ	1.99E-05	0.403 (126 °C) ⁿ
Methyl Stearate	C ₁₉ H ₃₈ O ₂	298.51	840 ^b	0.3554	443 ^f	64.99 ⁿ	4.13E-06	0.359 (139 °C) ⁿ

- a http://www.wolframalpha.com/entities/chemicals/methyl_nonanoate/zz/sv/zd/
b http://www.chemicalbook.com/ChemicalProductProperty_EN_CB6409834.htm
c <http://webbook.nist.gov/cgi/cbook.cgi?ID=C1731846&Units=SI&Mask=4#Thermo-Phase>
d <http://www.lookchem.com/Nonanoic-acid-9-oxo--methyl-ester/>
e <http://webbook.nist.gov/cgi/cbook.cgi?ID=C1732101&Units=SI&Mask=4#Thermo-Phase>
f <http://www.chemicaland21.com/lifescience/foco/METHYL%20STEARATE.htm>
g <http://webbook.nist.gov/cgi/cbook.cgi?Name=Methanol>
h <http://webbook.nist.gov/cgi/cbook.cgi?ID=C1731846&Units=SI&Mask=4#Thermo-Phase>
n <http://app.knovel.com/web/data-search.v>

4.5 Distillation design

The flow rates of feed materials were calculated based on the desired production and the mole fraction of each component. Materials were input into the system at room temperature under 1 atm. Operation pressure for each column was mainly determined based on the consideration of product thermal stability and condenser energy cost. Shin et al. [90] found that all FAMEs remained stable at 325 °C or below and FAME with shorter chain length or less double bond has higher thermal stability. However, the thermal stability data of dimethyl azelate and methyl 9-oxononanoate was not found from previous studies. Dimethyl azelate has a shorter chain length than main components of FAMEs, but has one more methyl group, therefore the comparison of thermal stability is not straight forward. Based on lab-scale distillation records, when the highest temperature reached to 195 °C, dimethyl azelate was still stable. Taking all these aspects into consideration, it was assumed that all the compounds remain stable under 280 °C.

For industrial vacuum distillation, the pressure can be as low as 10 mmHg [91] and therefore, this is the lower pressure limit for our distillation design. According to Cai et al. [92], in a trayed column the minimum dynamic pressure drop for a tray is in the order of 25 mmH₂O (0.036 psi). In this study, some data for pressure drop of hydrocarbon system from industrial distillation columns was presented, with the highest pressure drop of 0.16 psi. Based on this study, a pressure drop of 0.1 psi was assumed for the following design.

In Aspen Plus, RadFrac module was used to conduct distillation simulation. The stage number and feed stage for each column were initially assigned an estimated value. After these parameters are fixed, there are only two degrees of freedom left for calculation. We chose distillate rate and reflux ratio as the two parameters that need to

be specified. The starting value for distillate rate was the same as the mass flow rate of the target material from the feed stream, which means the recovery rate for product from distillate was 100%. The reflux ratio was given a temporary value 2.

Once the calculation was converged, we used “Design Specifications/Vary” function under each block to optimize the distillate rate and reflux ratio. Two parameters were input as design objectives which were usually the mass purity of the main product and the mass purity of the adjacent compound (in terms of volatility) in the product stream. The former input value was between 0.99 and 0.999, and the later value was around 0.001 to 0.01 depending on the separation difficulty for the product. The two unknown variables were distillate rate and reflux ratio. After the calculation was converged, the optimal values were output under each block.

The number of stage of a column and the reboiler reflux ratio are highly correlated. Once a column reaches to the minimum number of stages, the value of reflux ratio will turn to be infinity; therefore, the minimum number of stages can be calculated based on this theory. While slowly decreasing the stage number of each column, the “Vary” function for reflux ratio value would eventually output a very large number (e.g. bigger than 100), and that means the stage already reached to minimum. Two times of the minimum stage number was chosen for the final design of the column, and based on that, feed stage was optimized. This was determined by varying the feed stage starting from the middle of the column and choosing the one that leads to the lowest heat duty for condenser.

4.6 Results and discussion

4.6.1 Distillation design for separation of products obtained from ozonolysis in methanol

The design for the distillation process was based on the dimethyl azelate production of 4 tons/day, using four columns in total. Dimethyl azelate was chosen as the main target product in accordance with the primary research goal which is to develop biobased polymer, and dimethyl azelate can be used to synthesize biobased polyesters. According to the separation sequence as mentioned in section 4.3, methanol is separated from the top of the first column, while methyl hexanoate and methyl nonanoate is distilled as a mixture in the second column, with dimethyl azelate and the rest of the components coming from the bottom. The two parallel columns following the second column are responsible for separating all the other products including methyl hexanoate, methyl nonanoate and dimethyl azelate. The saturated esters and unknown compounds are separated together as a byproduct.

As shown in Figure 4.1, methanol comes out of the top of column B1 as DIS1 and its mass fraction is 0.999 with recovery of 0.999 according to Table 4.5. Methyl hexanoate and methyl nonanoate are separated from column B3 as distill and residue streams respectively, with purities of 0.99 and 0.981, recovery of 0.985 and 0.99. Column B4 purified dimethyl azelate with a mass fraction of 0.995 and recovery of 0.998 from the top stream. The purity for these products is specified in the “Design Specification” module, by automatically varying the value of distillate rate and reflux ratio, if the calculation in Aspen could converge, the design objective will be satisfied. When it doesn’t converge after several trials, the purity requirement has to be decreased slightly until conversion is achieved.

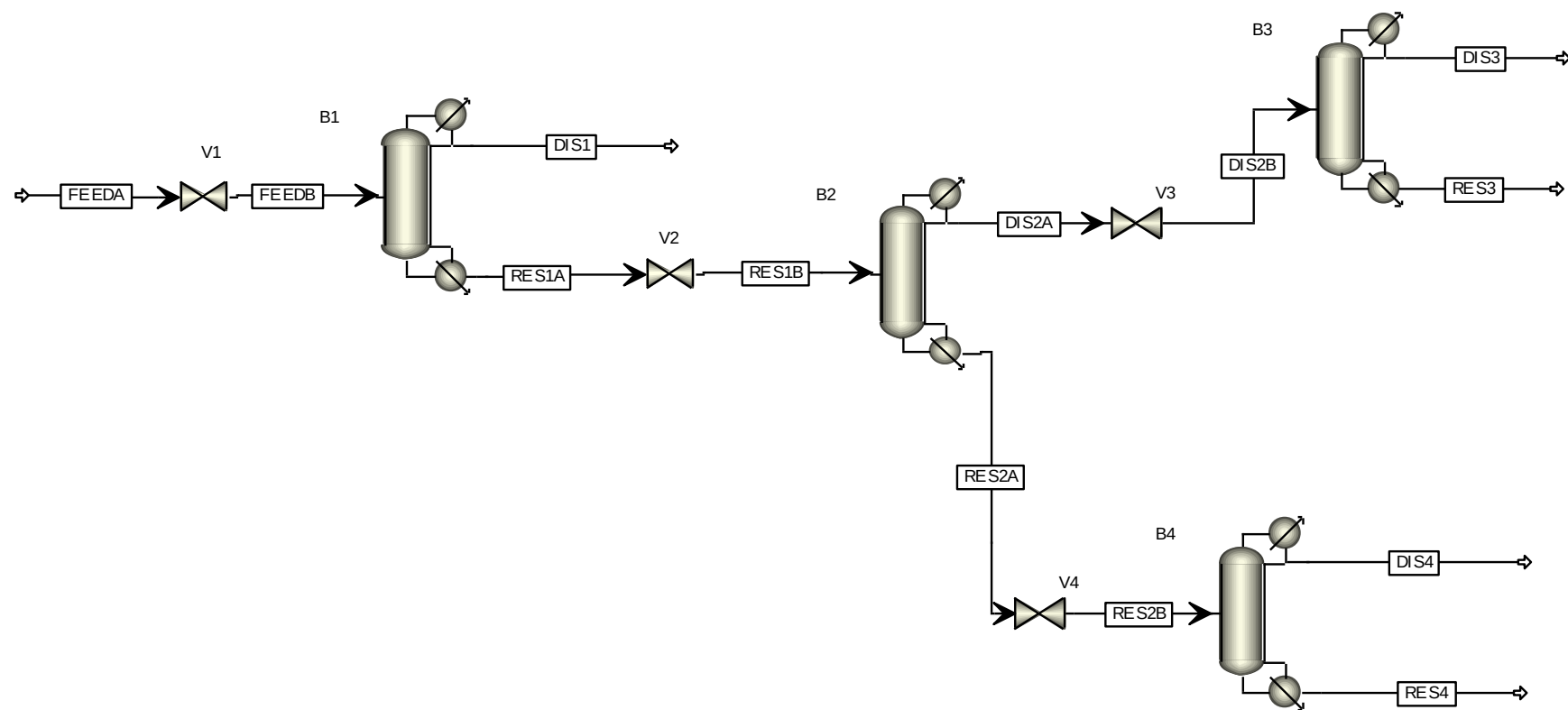


Figure 4.1 Distillation design in Aspen Plus for separating FAME ozonolysis products in methanol system. DIS1: methanol; DIS3: methyl hexanoate; RES3: methyl nonanoate; DIS4: dimethyl azelate; RES4: methyl palmitate and methyl stearate.

Table 4.5 Distillation results for the products from ozonolysis of FAMES in methanol*

	DIS1	DIS2A	DIS2B	DIS3	DIS4	FEEDA	FEEDB	RES1A	RES1B	RES2A	RES2B	RES3	RES4
	V3	B3			V1	B1	V2	B2	V4	B4			
	B1	B2	V3	B3	B4	V1	B1	V2	B2	V4	B4	B3	B4
	LIQUID	LIQUID	MIXED	LIQUID	LIQUID	LIQUID	LIQUID	LIQUID	MIXED	LIQUID	MIXED	LIQUID	LIQUID
Substream: MIXED													
Mole Flow mol/hr													
1-HEX-01	3.245856	605.7756	605.7756	599.7179	4.22E-07	609.0214	609.0214	605.7756	605.7756	4.22E-07	4.22E-07	6.057714	2.06E-14
1-NON-01	1.23E-11	254.5184	254.5184	1.980124	0.681747	255.2001	255.2001	255.2001	255.2001	0.681752	0.681752	252.5383	4.72E-06
METHA-01	10135.86	10.1458	10.1458	10.14564	0	10146.01	10146.01	10.1458	10.1458	7.28E-19	7.28E-19	1.65E-04	0
METHY-01	2.31E-32	2.97E-08	2.97E-08	8.62E-28	2.757977	127.9322	127.9322	127.9322	127.9322	127.9322	127.9322	2.97E-08	125.1742
METHY-02	1.96E-39	5.80E-12	5.80E-12	1.13E-35	3.47E-05	44.2197	44.2197	44.2197	44.2197	44.2197	44.2197	5.80E-12	44.21967
DMA	9.76E-28	0.52241	0.52241	3.42E-11	900.5842	902.008	902.008	902.0081	902.0081	901.4857	901.4857	0.52241	0.901497
Mole Frac													
1-HEX-01	3.20E-04	0.695525	0.695525	0.980182	4.67E-10	0.050397	0.050397	0.311408	0.311408	3.93E-10	3.93E-10	0.023378	1.21E-16
1-NON-01	1.21E-15	0.292227	0.292227	3.24E-03	7.54E-04	0.021118	0.021118	0.131189	0.131189	6.35E-04	6.35E-04	0.974605	2.77E-08
METHA-01	0.99968	0.011649	0.011649	0.016582	0	0.839596	0.839596	5.22E-03	5.22E-03	6.77E-22	6.77E-22	6.38E-07	0
METHY-01	2.28E-36	3.41E-11	3.41E-11	1.41E-30	3.05E-03	0.010587	0.010587	0.065765	0.065765	0.119082	0.119082	1.14E-10	0.735042
METHY-02	1.94E-43	6.66E-15	6.66E-15	1.86E-38	3.84E-08	3.66E-03	3.66E-03	0.022732	0.022732	0.041161	0.041161	2.24E-14	0.259665
DMA	9.63E-32	6.00E-04	6.00E-04	5.59E-14	0.996195	0.074642	0.074642	0.46369	0.46369	0.839123	0.839123	2.02E-03	5.29E-03
Mass Flow kg/hr													
1-HEX-01	0.325107	60.6749	60.6749	60.06815	4.23E-08	61	61	60.6749	60.6749	4.23E-08	4.23E-08	0.606745	2.06E-15
1-NON-01	1.75E-12	36.20303	36.20303	0.281655	0.096973	36.3	36.3	36.3	36.3	0.096973	0.096973	35.92137	6.71E-07
METHA-01	324.7749	0.325093	0.325093	0.325088	0	325.1	325.1	0.325093	0.325093	2.33E-20	2.33E-20	5.30E-06	0
METHY-01	6.25E-33	8.02E-09	8.02E-09	2.33E-28	0.745911	34.6	34.6	34.6	34.6	34.6	34.6	8.02E-09	33.85409
METHY-02	5.86E-40	1.73E-12	1.73E-12	3.39E-36	1.04E-05	13.2	13.2	13.2	13.2	13.2	13.2	1.73E-12	13.19999
DMA	1.82E-28	0.097299	0.097299	6.37E-12	167.7348	168	168	168	168	167.9027	167.9027	0.097299	0.167905
Mass Frac													
1-HEX-01	1.00E-03	0.623584	0.623584	0.99	2.51E-10	0.095581	0.095581	0.193788	0.193788	1.96E-10	1.96E-10	0.016566	4.37E-17
1-NON-01	5.39E-15	0.372075	0.372075	4.64E-03	5.75E-04	0.056879	0.056879	0.115937	0.115937	4.49E-04	4.49E-04	0.980777	1.42E-08
METHA-01	0.999	3.34E-03	3.34E-03	5.36E-03	0	0.509401	0.509401	1.04E-03	1.04E-03	1.08E-22	1.08E-22	1.45E-07	0
METHY-01	1.92E-35	8.25E-11	8.25E-11	3.84E-30	4.42E-03	0.054215	0.054215	0.110508	0.110508	0.160334	0.160334	2.19E-10	0.716914
METHY-02	1.80E-42	1.78E-14	1.78E-14	5.58E-38	6.15E-08	0.020683	0.020683	0.042159	0.042159	0.061168	0.061168	4.73E-14	0.279531
DMA	5.59E-31	1.00E-03	1.00E-03	1.05E-13	0.995	0.26324	0.26324	0.53657	0.53657	0.778049	0.778049	2.66E-03	3.56E-03
Total Flow mol/hr	10139.11	870.9622	870.9622	611.8437	904.0239	12084.39	12084.39	1945.282	1945.282	1074.319	1074.319	259.1185	170.2954
Total Flow kg/hr	325.1	97.30032	97.30032	60.6749	168.5777	638.2	638.2	313.1	313.1	215.7997	215.7997	36.62542	47.22199
Total Flow cum/hr	0.436919	0.132459	0.132459	0.080712	0.167436	0.746372	0.746372	0.386715	0.386715	0.251177	0.251177	0.051851	0.07943
Temperature C	64.54242	111.7358	105.7677	87.42967	203.7664	30	30.00667	174.8753	161.9659	247.7904	239.4114	152.8729	278.9174
Pressure atm	1	0.5	0.4	0.3	0.2	1.4	1.2	1.095264	0.6	0.629287	0.5	0.361241	0.308874
Vapor Frac	0	0	0.04066	0	0	0	0	0	0.12846	0	0.072696	0	0
Liquid Frac	1	1	0.95934	1	1	1	1	1	0.87154	1	0.927304	1	1
Solid Frac	0	0	0	0	0	0	0	0	0	0	0	0	0
Enthalpy Btu/lbmol	-1.01E+05	-1.25E+05	-1.25E+05	-1.19E+05	-2.74E+05	-1.23E+05	-1.23E+05	-2.09E+05	-2.09E+05	-2.69E+05	-2.69E+05	-1.40E+05	-2.74E+05
Enthalpy Btu/lb	-3144.77	-1119.95	-1119.95	-1197.33	-1471.11	-2325.14	-2325.14	-1299.54	-1299.54	-1338.72	-1338.72	-988.777	-986.84
Enthalpy Btu/hr	-2.25E+06	-2.40E+05	-2.40E+05	-1.60E+05	-5.47E+05	-3.27E+06	-3.27E+06	-8.97E+05	-8.97E+05	-6.37E+05	-6.37E+05	-79839.1	-1.03E+05
Entropy Btu/lbmol-R	-54.6065	-150.178	-150.167	-133.647	-199.048	-81.959	-81.958	-186.785	-186.715	-210.469	-210.447	-193.018	-313.362
Entropy Btu/lb-R	-1.70305	-1.34429	-1.34418	-1.34769	-1.06742	-1.5519	-1.55188	-1.16049	-1.16005	-1.04778	-1.04767	-1.36557	-1.13007
Density lbmol/cuft	1.448699	0.410485	0.019126	0.473241	0.337063	1.010761	1.010752	0.31403	8.11E-03	0.267013	0.010056	0.311973	0.133843
Density lb/cuft	46.45104	45.85768	2.136623	46.93003	62.85384	53.38024	53.37978	50.54419	1.305177	53.63523	2.019905	44.09618	37.11396
Average MW	32.06397	111.7159	111.7159	99.16732	186.4748	52.81194	52.81194	160.9536	160.9536	200.8711	200.8711	141.3462	277.2946
Liq Vol 60F cum/hr	0.409224	0.118702	0.118702	0.074217	0.136304	0.71862	0.71862	0.309396	0.309396	0.190695	0.190695	0.044484	0.05439

* 1-HEX-01: Methyl hexanoate; 1-NON-01: Methyl nonanoate; METHA-01: Methanol; METHY-01: Methyl palmitate; METHY-02: Methyl stearate; DMA: Dimethyl azelate.

Operating pressure for column B1 is the highest among all the columns, which is about 1 atm. The reason is methanol is much more volatile than methyl hexanoate, so it can be separated under atmospheric pressure and at lower temperatures. Pressure for column B2 is around 0.5 atm, and B3 is between 0.3 and 0.36 atm. This design was based on the consideration of the lower volatility of methyl hexanoate and methyl nonanoate, as at lower pressure the operation temperature is also lower, it will reduce the energy cost for the condenser. Since dimethyl azelate as well as the other two heavier saturated FAMES are less stable than the other products separated in previous columns, the column for separating dimethyl azelate (B4) is run under the lowest pressure which is between 0.2 and 0.3 atm.

Table 4.6 shows the simulation results for reboiler and condenser. As indicated by the table, column B1 has the highest heat duty value. The reason for this is that methanol takes more than 60% in molar ratio in the total mixture and therefore it requires much more energy to be removed. The distillation rate for column B1, B3 and B4 are almost equal to the feed rate of methanol, methyl hexanoate and methyl nonanoate, which indicates that the products were recovered with high rate. Reflux ratio is related to the number of stages and will increase if the stage number is decreased. In this design since twice of the minimum number of stages was chosen as the specification, the reflux ratio was determined by that.

Table 4.6 Reboiler and condenser design specification for separating products from ozonolysis of FAMES in methanol

	Reboiler				
Name	Temperature	Heat duty	Distillate rate	Reflux rate	Reflux ratio
Units	°C	Btu/hr	mol/hr	mol/hr	
B1	64.542419	-396828.13	10139.1075	1725.44119	0.170176832
B2	111.735738	-51219.8979	870.962411	294.894087	0.338584172
B3	87.429614	-39455.7231	611.843845	453.059307	0.740481924
B4	203.76638	-84399.1429	904.023843	591.083631	0.65383633
	Condenser				
Name	Temperature	Heat duty	Bottoms rate	Boilup rate	Boilup ratio
Units	°C	Btu/hr	mol/hr	mol/hr	
B1	174.875332	517311.533	1945.28156	10709.717	5.50548425
B2	247.790382	71106.5553	1074.31924	1277.80933	1.18941305
B3	152.872912	39694.8148	259.118566	841.015965	3.24568007
B4	278.917162	71826.9239	170.295402	1038.05137	6.09559248

The number of stages will reflect the difficulty for separation given the requirement for the purity of products. In this process, the higher number of stages appears in column B2 and column B4. B2 is used to separate methyl hexanoate and methyl nonanoate from dimethyl azelate and B4 is designed to separate dimethyl azelate from methyl palmitate. Both of the two separations are more difficult than the other ones by simply comparing the boiling point data in Table 4.4.

Table 4.7 Distillation column design specification for separating products from ozonolysis of FAMES in methanol

Name	Stages	Feed Stage	Tray Spacing	Height	Diameter
Units			m	m	m
B1	15	10	0.2	3.12	0.4925
B2	20	9	0.2	4.32	0.2262
B3	10	6	0.2	1.92	0.1976
B4	17	12	0.2	3.6	0.2969

Feed stage was optimized by choosing the one that gives the minimum cooling duty for the condenser. The initial guess for the feed stage was the middle stage of the column, while varying the number by increasing or decreasing it the minimum cooling duty appeared after several trials. As listed in Table 4.7, the optimal feed stage is close to but not always the middle stage. Since the amount of production specified in this study is not very high, a small spacing was defined so the column will not be too tall and thin.

4.6.2 Distillation design for products obtained from ozonolysis in water

Design for the distillation for separating products obtained from ozonolysis of FAMES in water system is simpler than that for the methanol system products. The reason is that no solvent is present in this mixture, so only 3 columns are required instead of 4. As indicated in Figure 4.2, the first column separates hexanal and nonanal from the rest of the materials. Following the first column, two parallel columns separate hexanal, nonanal and methyl 9-oxononanoate respectively and leave the two saturated esters as a byproduct

mixture. This design was based on hexanal productivity of 1 ton/day. The reason for this assumption is that based on the same amount input of FAMES, the ratio of mass yield of dimethyl azelate from methanol system to that of hexanal from water system is about 3.8:1; since dimethyl azelate and hexanal are primary products from the two reactions respectively and dimethyl azelate productivity was assumed 4 tons/day in the previous design, production of hexanal was chosen as 1 ton/day for comparison.

The separation results are shown in Table 4.8. The product hexanal came from column C2 as D2 with a mass fraction of 0.999 with recovery of 0.993, and nonanal was separated from the same column as R2 with a lower mass purity of 0.966 and recovery of 0.992. Column C3 was responsible for the purification of methyl 9-oxononanoate which was recovered with a mass ratio of 0.99 and recovery of 0.993. The purity of nonanal is relatively lower because we wanted to guarantee the purity of methyl 9-oxononanoate, however, at the same time more methyl 9-oxononanoate was also lost in the nonanal stream. As shown in Table 4.8, the mass fraction of methyl 9-oxononanoate was 0.025 in stream R2.

Low pressure was also applied for this distillation process, for example, C1 was under pressure 0.3 atm, C2 under 0.2 atm and C1 under around 0.1 atm. The pressure for downstream columns is lower than upstream for two reasons: 1) to save the cost from using pumps (because the pressure of output stream from the previous column will be higher than the operating pressure of feed stage in the next column so no pump is needed to increase the pressure of feed stream) and to reduce the separation temperature so that heavy compounds can be protected from decomposing.

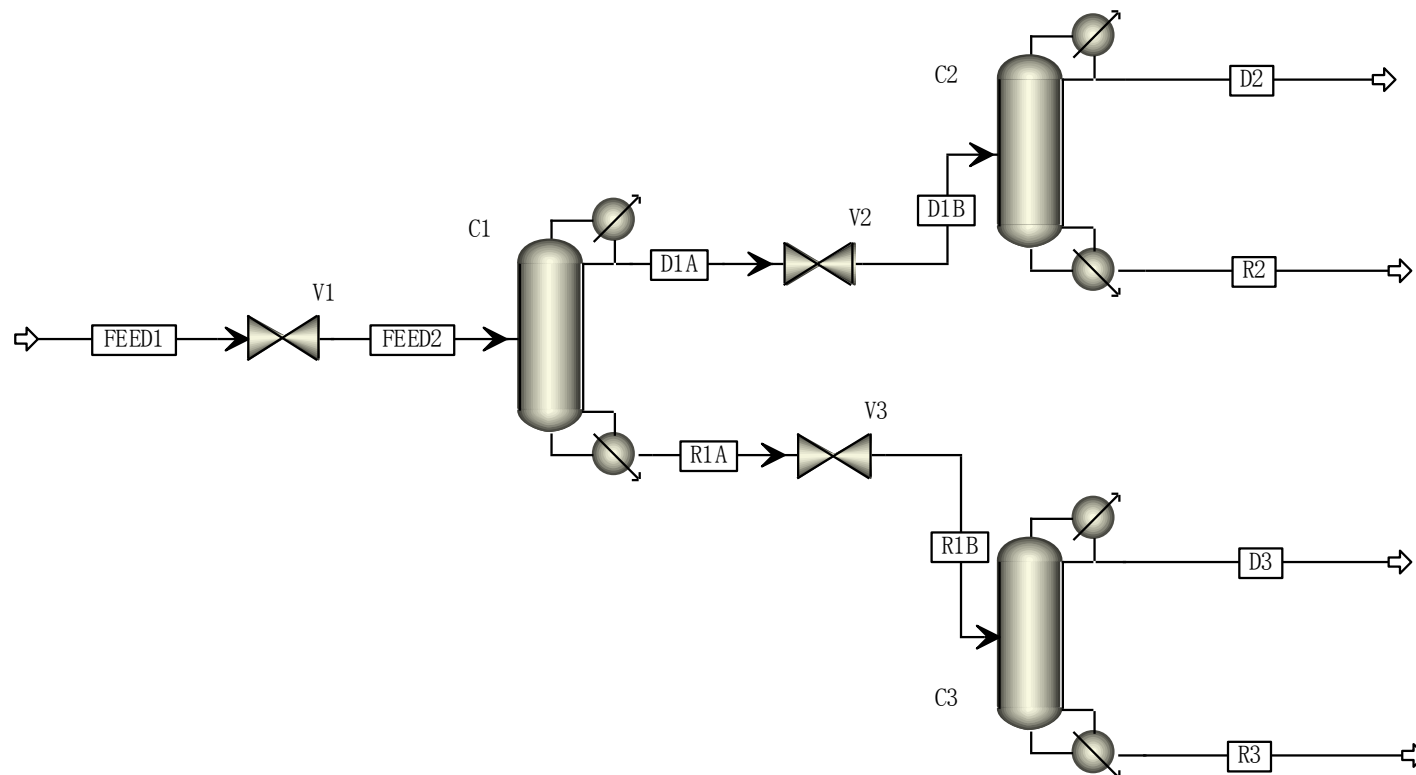


Figure 4.2 Distillation design in Aspen Plus for products made in water using ozonolysis. D2: hexanal; R2: nonanal; D3: methyl 9-oxononanoate; R3: methyl palmitate and methyl stearate.

Table 4.8 Distillation result for products from ozonolysis in water*

	D1A	D1B	D2	D3	FEED1	FEED2	R1A	R1B	R2	R3
	V2	C2			V1	C1	V3	C3		
	C1	V2	C2	C3	V1	V1	C1	V3	C2	C3
	LIQUID	MIXED	LIQUID	LIQUID	LIQUID	LIQUID	LIQUID	MIXED	LIQUID	LIQUID
Substream: MIXED										
Mole Flow kmol/hr										
1-HEX-01	0.416331	0.416331	0.4135592	4.04E-12	0.416331	0.416331	4.04E-12	4.04E-12	2.77E-03	2.32E-19
1-NON-01	0.1935185	0.1935185	2.92E-04	1.22E-03	0.1947395	0.1947395	1.22E-03	1.22E-03	0.193227	7.97E-09
M-9OXO	3.75E-03	3.75E-03	5.03E-17	0.6742244	0.6786536	0.6786536	0.6748993	0.6748993	3.75E-03	6.75E-04
M-PALM	3.26E-11	3.26E-11	3.76E-39	4.05E-03	0.1279322	0.1279322	0.1279322	0.1279322	3.26E-11	0.123885
M-STEА	4.47E-15	4.47E-15	5.01E-49	6.16E-07	0.0442197	0.0442197	0.0442197	0.0442197	4.47E-15	0.044219
Mole Frac										
1-HEX-01	0.6785013	0.6785013	0.9992956	5.94E-12	0.2847923	0.2847923	4.76E-12	4.76E-12	0.0138761	1.38E-18
1-NON-01	0.3153801	0.3153801	7.04E-04	1.80E-03	0.133212	0.133212	1.44E-03	1.44E-03	0.9673288	4.72E-08
M-9OXO	6.12E-03	6.12E-03	1.22E-16	0.9922461	0.4642347	0.4642347	0.7956164	0.7956164	0.018795	4.00E-03
M-PALM	5.32E-11	5.32E-11	9.10E-39	5.96E-03	0.0875123	0.0875123	0.150815	0.150815	1.63E-10	0.7340073
M-STEА	7.29E-15	7.29E-15	1.21E-48	9.07E-07	0.0302485	0.0302485	0.0521291	0.0521291	2.24E-14	0.2619939
Mass Flow kg/hr										
1-HEX-01	41.7	41.7	41.42237	4.05E-10	41.7	41.7	4.05E-10	4.05E-10	0.2776255	2.33E-17
1-NON-01	27.52633	27.52633	0.0414643	0.1736737	27.7	27.7	0.1736749	0.1736749	27.48486	1.13E-06
M-9OXO	0.6992568	0.6992568	9.37E-15	125.575	126.4	126.4	125.7007	125.7007	0.6992568	0.1257007
M-PALM	8.82E-09	8.82E-09	1.02E-36	1.094577	34.6	34.6	34.6	34.6	8.82E-09	33.50542
M-STEА	1.33E-12	1.33E-12	1.50E-46	1.84E-04	13.2	13.2	13.2	13.2	1.33E-12	13.19982
Mass Frac										
1-HEX-01	0.5963483	0.5963483	0.999	3.19E-12	0.1711823	0.1711823	2.33E-12	2.33E-12	9.75E-03	4.97E-19
1-NON-01	0.3936517	0.3936517	1.00E-03	1.37E-03	0.113711	0.113711	1.00E-03	1.00E-03	0.9656774	2.42E-08
M-9OXO	0.01	0.01	2.26E-16	0.99	0.5188834	0.5188834	0.7237724	0.7237724	0.0245683	2.68E-03
M-PALM	1.26E-10	1.26E-10	2.46E-38	8.63E-03	0.1420361	0.1420361	0.1992234	0.1992234	3.10E-10	0.7154548
M-STEА	1.91E-14	1.91E-14	3.61E-48	1.45E-06	0.0541871	0.0541871	0.0760042	0.0760042	4.69E-14	0.281861
Total Flow kmol/hr	0.6136039	0.6136039	0.4138507	0.6794931	1.461876	1.461876	0.8482721	0.8482721	0.1997532	0.168779
Total Flow kg/hr	69.92558	69.92558	41.46384	126.8435	243.6	243.6	173.6744	173.6744	28.46174	46.83094
Total Flow l/min	1.539877	1.540002	0.892541	1.9403	4.282013	4.282013	3.236708	354.0339	0.6527915	1.086376
Temperature C	88.36302	88.36302	61.83982	139.3845	30	30.00001	226.3106	210.1464	134.6971	269.6369
Pressure bar	0.20265	0.20265	0.101325	0.020265	0.303975	0.303975	0.3336504	0.20265	0.1909568	0.0823178
Vapor Frac	0	8.26E-08	0	0	0	0	0	0.1264302	0	0
Liquid Frac	1	0.9999999	1	1	1	1	1	0.8735698	1	1
Solid Frac	0	0	0	0	0	0	0	0	0	0
Enthalpy cal/mol	-71957.75	-71957.75	-67406.44	-1.58E+05	-1.30E+05	-1.30E+05	-1.52E+05	-1.52E+05	-80644.74	-1.52E+05
Enthalpy cal/gm	-631.4364	-631.4364	-672.784	-846.744	-777.2402	-777.2402	-740.8897	-740.8897	-565.9893	-547.6892
Enthalpy cal/sec	-12264.88	-12264.88	-7748.946	-29834.43	-52593.26	-52593.26	-35742.66	-35742.66	-4474.734	-7124.667
Entropy cal/mol-K	-157.0764	-157.0764	-138.7853	-212.4984	-223.9689	-223.9689	-224.918	-224.8554	-197.4914	-337.795
Entropy cal/gm-K	-1.378361	-1.378361	-1.385217	-1.138342	-1.344067	-1.344067	-1.098559	-1.098254	-1.386055	-1.217415
Density mol/cc	6.64E-03	6.64E-03	7.73E-03	5.84E-03	5.69E-03	5.69E-03	4.37E-03	3.99E-05	5.10E-03	2.59E-03
Density gm/cc	0.7568307	0.7567696	0.7742658	1.089552	0.9481522	0.9481522	0.8942956	8.18E-03	0.7266675	0.718458
Average MW	113.9588	113.9588	100.1903	186.6737	166.6352	166.6352	204.739	204.739	142.4846	277.469
Liq Vol 60F l/min	1.417068	1.417068	0.8451901	1.711824	3.99096	3.99096	2.573892	2.573892	0.5718774	0.8620683

* 1-HEX-01: Hexanal; 1-NON-01: Nonanal; M-9OXO: Methyl 9-oxononanoate; M-PALM: Methyl palmitate; M-STEА: Methyl stearate.

Table 4.9 Reboiler and condenser design specification for products from ozonolysis in water

	Reboiler				
Name	Temperature	Heat duty	Distillate rate	Reflux rate	Reflux ratio
Units	°C	Btu/hr	mol/hr	mol/hr	
C1	88.363021	-2209.78869	0.613603904	0.070668387	0.115169389
C2	61.8398209	-1380.98729	0.413850746	0.105092911	0.253939159
C3	139.384487	-3639.2395	0.679493113	0.178110906	0.262123195
	Condenser				
Name	Temperature	Heat duty	Bottoms rate	Boilup rate	Boilup ratio
Units	°C	Btu/hr	mol/hr	mol/hr	
C1	226.310557	6795.50243	0.848272141	1.67028069	1.96903872
C2	134.697143	1422.18368	0.199753158	0.418675701	2.09596536
C3	269.636922	2422.80584	0.168779028	0.372716149	2.20830842

The heat duty for this distillation process (Figure 4.9) is significantly lower compared to the one designed to separate products of ozonolysis of FAMES in the methanol system. Firstly, this observation can be explained by the fact that the mass productivity for this process is much lower (almost 25% of the previous process for ozonolysis products obtained in methanol system). Secondly, there is no solvent that needs to be separated, which constituted a substantial fraction of the feed in the methanol system. Besides, reflux ratio can also affect the heat duty, since lower reflux means less material will go back to the column and thus less heat will be spent on repeatedly heating or cooling.

Compared to the previous process the reflux ratios for the reboiler in this process are much lower, so the heat duty was also reduced.

The stage number was also determined by doubling the number of minimum stages and feed stage was optimized by the same method. Tray spacing was also the same as the former process. Table 4.10 shows that column C1 has the highest stage number and C3 has the lowest, this may be because the difference between boiling point of nonanal and methyl 9-oxononanoate (58.4 °C) is slightly smaller than that between hexanal and nonanal (60 °C), and between methyl 9-oxononanoate and methyl palmitate (167.6 °C).

Table 4.10 Distillation column design specification for products from ozonolysis in water

Name	Stages	Feed Stage	Tray Spacing	Height	Diameter
Units			m	m	m
C1	20	8	0.2	4.32	0.2975
C2	14	9	0.2	2.88	0.1742
C3	10	5	0.2	1.92	0.3699

The profiles from both of the two distillation processes based on the same hourly input of FAMEs (360.7 Kg/hr) were summarized and compared in Table 4.11 in terms of purity, mass yield, recovery and the heat duty of reboilers and condensers. It is shown that most final products have a very high purity (> 0.99) except methyl nonanoate (0.981) and nonanal (0.966). This happened was because we gave higher priority of purity to dimethyl azelate than methyl nonanoate and to methyl 9-oxononanoate than nonanal when separating the neighbor compounds, as we assumed the two products may be more

valuable. The recoveries of the products are all between 0.98 and 0.999, which means that most of the product was recovered during the distillation. The biggest difference resides in the heat duty of the reboilers and the condensers. The heat duty of the methanol system distillation process is more than 70 times of the water system process. This was caused by the existence of the methanol in the first system, and if we exempt the heat duty from the columns for separating methanol (column B1), the heat duty ratio of the first distillation process to the second process dropped to about 20 : 1. From this we conclude that the distillation cost for the water system ozonolysis products cost much less in terms of the energy consumption, and considering the number of distillation column required for the methanol system products is also larger than the water system products, the overall cost of the separation of water system products is much more advantageous.

Table 4.11 Comparison of two distillation processes based on the same input of FAMES*

Systems	Products	Product purity	Product flow rate (Kg/hr)	Mass yield (Kg/100 Kg)	Recovery	Heat duty (Btu/hr)
Methanol	Methyl hexanoate	0.990	60.07	14.02	0.985	1271842.72
	Methyl nonanoate	0.981	35.92	8.30	0.990	
	Dimethyl azelate	0.995	167.73	39.45	0.998	
Water	Hexanal	0.999	41.42	11.46	0.993	17870.51
	Nonanal	0.966	27.48	7.63	0.992	
	Methyl 9-oxononanoate	0.990	125.58	34.76	0.993	

* Input flow rate of FAMES was 360 Kg/hr, which was 8.6 tons/day.

4.7 Conclusion

In this chapter two distillation processes for separating two sets of ozonolysis products were designed for a small industrial operation and evaluated with simulation results. Distillation sequence was firstly determined by heuristic method by taking in consideration the molar fraction, thermal stability and the reactivity of the materials. Based on this sequence, the distillation columns were designed with specification of stage number, dimension, operating temperature and pressure, reflux ratio and the optimal feed stage. Most of the purity of products from the two distillation processes are higher than 0.99, except for methyl nonanoate (0.981) in methanol system and nonanal (0.966) in water system. Recovery of main products are also satisfactorily higher than 0.98.

Comparing the two processes, it was found that the heat duty spent on separating ozonolysis products from water system was much lower than that for products from methanol system, even after considering the difference between the productions. The reason was that the products from the water system do not contain solvent and also the compounds were more volatile in average.

Considering the yields of reaction, as well as the separation result and energy consumption of distillation for both ozonolysis process in methanol and water, the water system is more economical as far as separations is concerned and should be recommended for industrial development.

Chapter 5: Simulation of Wiped Film Distillation in Aspen Plus

5.1 Introduction

Molecular distillation, according to G. Burrows (1960), is a type of short-path distillation under a high vacuum [93]. High vacuum is applied to reduce the obstruction exerted by the air, and the short path between the central condenser and the surrounded heating surface is used to ease the condensation process for the product vapor molecules. However, high vacuum for molecular distillation is not always applied and it depends on the materials, for example, in this project the pressure was set between 0.03 atm and 1 atm.

There are three different types of molecular evaporators, which differ by the way the film is formed. These are 1) falling film evaporator, 2) centrifugal film evaporator and 3) wiped film evaporator. Falling film evaporator was the first to be introduced among the three types. Falling film evaporators work using gravity that drives the feed down along the evaporator wall. During this process, a film is naturally formed on the internal surface of the jacket. However the disadvantage of this evaporator is that the film is not evenly spread, especially for high-viscosity material. To compensate this drawback of falling film evaporator, the wiped film evaporator was designed and patented in the 1960s [94]. The modification was done by installing a wiper, which consists of several tubes or blades fastened on a circular frame nested inside the column. When the wiper rotates, the liquid material will be evenly spread on the wall.

Wiped film distillation (WFD) is widely used to separate many materials in industry especially for sensitive materials, such as natural pigment, vitamins, essential oil and

polyunsaturated fatty acids, because it has a short residence time, high heat transfer efficiency and good ability in handling viscous fluids [95].

WFD has been used for more than half century, however, simulation study on it is still not mature. Most of the available research was conducted on falling film distillation, because it is easier to describe with numerical equations [96]. However, according to former studies on wiped film distillation, two ways were applied to set up the model. One is a numerical method, which was firstly developed by Kern and Karakas (1958), who developed the design equations based on heat and mass transfer, hydrodynamics and rheology principles to explain wiped film distillation [97]. Later, Li et al. (2006) studied the fluid mass transfer and heat transfer in wiped film evaporator using a 2 dimensional model solved numerically [98]. More recently, in S. Zeboudj's research, the liquid flow in a wiped film evaporator was represented by the model of a series of paralleled mixed cells with dead zone, and the model was developed using the DTS Pro software [99]. The alternative non-numerical approach is to simulate WFD in a flash evaporator. G. Gruber in 1989 modeled the separation of a complex final product with ASPEN by assuming it as a multiple-stage flash [100]. By inputting Fortran code into Aspen, the author was able to predict the purity and recovery of the product. However, no detailed results showed how good the model can fit the experimental data, neither the effect from the operating conditions. In general, a body of study has been done in this area for tens of years, which could not satisfy the correspondence of experimental data and universality in application. Moreover, most studies were conducted based on 2 or 3 components in relatively simple systems [101], which reduced the complexity of the model.

The aim of this study is to develop a model using ASPEN to simulate the separation process of WFD for 3 different multi-component systems and then compare the modeling result with experimental data to demonstrate the accuracy of the simulation and the method.

Aspen Plus is a well know software for separation design, chemical processing simulation and optimization, as well as property analysis and estimation, and it has been widely used in industry for over 25 years. Since it is a well-developed simulation tool with up-to-date databanks, it can be reliably integrated in a plant simulation along with other unit operations.

Unlike fractional distillation, WFD is not an equilibrium process, and the system in the column is not homogeneous either. Temperature on the wall side is much higher than that on the condenser side and thus, the partial pressure for the material on different sides is also different. Due to this difference, molecules are driven from the heating wall to the condenser, and on the other hand, the driving force is also strengthened by the process of condensation. However, according to Burrows [93], if we take the whole process of continuous molecular distillation as an entity, it is similar to regular distillation (e. g. flash separation) based on the fact that it follows Raoult's law, which means the partial vapor pressure of each component in the mixture is equal to the vapor pressure of the pure component multiplied by its mole fraction in the mixture. No substantial literature was found on equilibrium simulation of WFD, like the earliest study conducted by Gruber [100] in 1989, who simulated WFE in Aspen Plus as a series of co-current flash tanks, where the material were assumed following through a series of flash evaporators successively until the calculated vapor and liquid composition reached to steady value.

The total amount of distillates exiting from all of the flash evaporators was equaled to the vapor stream in original data. Liquid entrainment was described as a function of vapor velocity, heat transfer coefficient as a function of hot oil flow rate and temperature, and heat loss as a function of ambient temperature using Fortran code. However, as mentioned previously, no comparison between modeling and experimental data was shown in this publication, and no information about operating pressure was mentioned. Jacinto Lopez-Toledo [101] also performed studies on equilibrium simulation of WFD and assumed the wiped film evaporator as a one-stage flash separator. Corresponding equations consisting of flash mass balance and heat transfer coefficient were developed and an Excel-based program was built to do solve the equations. Three different 2-component mixtures were used to verify the model, with relative errors that varied between -20% and 20%. Similar to the study by Gruber [100], this paper also didn't give much emphasis to the impact of pressure on the separation efficiency. Chuaprasert introduced a data reconciliation process of an agitated thin film evaporator using Aspen Plus in 1999 [102], and this model consisted of one heat exchanger and one flash separator, and an objective function containing multiple variables was chosen to be minimized. This model could increase the fit between measured values and the process model by about 60%. The evaporator used in that study is different from what is presented herein, as that study used an external condenser, and the evaporation temperature and pressure were not included as independent variables.

5.2 Experiment

5.2.1 Materials

The two-component mixture was prepared by mixing methanol and methyl hexanoate (> 99.9% mass fraction) in two mass ratios: 27:73 and 51:49. Methyl ester mixture was generated from ozonolysis of soybean FAMES, in which 7 main components take up more than 90% mass fraction. The composition in mass was: methanol: 21.4%, water 3.8%, methyl hexanoate 11.5%, methyl nonanoate 7.7%, dimethyl azelate 33.2%, methyl palmitate 8.6%, methyl stearate 3.4% and impurity 10.4%. FAMES were obtained from Zeeland Inc., and the mass fraction for each component is: methyl palmitate 10.1%, methyl stearate 4.2%, methyl oleate 21.9%, methyl linoleate 51.7%, methyl linolenate 6.8% and impurity 5.3%.

5.2.2 Analytical methods

Quantitative analysis was conducted using the same gas chromatography machine as described in Chapter 2, with the same capillary column as well as the same carrier and makeup gas. Sample prepared from ozonolysis was analyzed with this method: injector and detector temperature were set up at 250 °C; column temperature initially started at 50 °C, after 2mins, it slowly increased to 240 °C at a rate 5 °C/min and stayed for 2 mins. For methanol and methyl hexanoate system, a similar method was applied except for the terminal temperature, which was 100 °C instead of 240 °C. For FAMES, the analysis was run using EN14103 FAME content method (Agilent Technologies) [103].

5.2.3 Wiped film distillation

Wiped film distillation was carried out using ICL-04A wiped film evaporator (by InCon Processing, L.L.C.). The flow rate of feed was varied between 0.1 and 2 L/hr; temperature was set between room temperature (25 °C) and 300 °C and the operating temperature applied was in a range of 20 mmHg to 760 mmHg. As shown in Table 5.1 and Figure 5.1, the height of the evaporator (A) is 23.1 cm, and the inner diameter is 9.6 cm, with the total capacity of 0.987 L. The heating area (A-3) covered a height of 19.1 cm, which has the same height as the 3-tube wiper (A-2), while the condenser finger (A-6) is about 2 cm shorter than them. The external diameters of the condenser and the wiper are 2.3 cm and 1.3 cm respectively. According to Figure 5.1, material to be separated was supplied by a peristaltic pump (C) into the column, and then it fell down under the force of gravity, once the liquid reached to the area contacting with wipers, it was spread evenly on to the inner surface of wall. At the same time, the mixture was heated up by the internal wall that was in contact with circulating hot oil from the jacket (controlled by Thermal H350 from Julabo Inc.). Some fraction of the mixture was evaporated and part of the vapor molecules would be condensed when they reach the surface of the condenser (operated by circulating cooling water). Condenser temperature was kept at 3 °C constantly to insure high condensation efficiency. Two flasks were connected to the column to collect distillate and residue.

Table 5.1 Dimensions of ICL-04 wiped film evaporator

Element	Total Column			Heating Area	Condenser		Wiper		
Dimension	Height	V	ID	Height	Height	ED	Height	ED	No.
Unit	cm	L	cm	cm	cm	cm	cm	cm	
Value	23.1	0.987	9.6	19.1	17.2	2.3	19.1	1.3	3

*ID: Inner diameter; ED: External diameter.

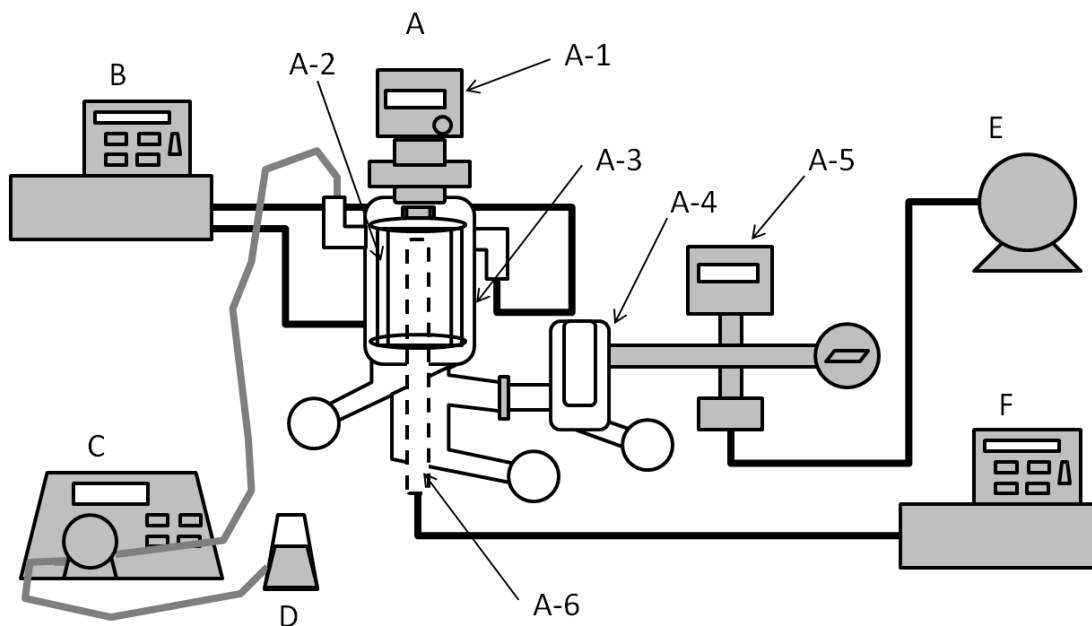


Figure 5.1 Wiped film evaporator and adjunctive facilities. A. Wiped film evaporator; A-1. Rolling speed meter; A-2. Wiper; A-3. Heating area; A-4. Dry ice trap; A-5. Pressure gage; A-6. Condenser; B. Oil heating system; C. Peristaltic Pump; D. Material container; E. Vacuum pump; F. Water cooling system.

5.2.4 Simulation in Aspen Plus

In Aspen Plus, FLASH2 was used to set up a one-stage flash separation process to simulate WFD, and the process was adiabatic. Since there are many parameters that can affect separation result in WFD than in flash process, some parameters were fixed in WFD. In this study, the volumetric flow rate, temperature and pressure of the feedstock were fixed; the rolling speed of the wiper and cooling temperature in condenser were also fixed. Detailed values for these parameters will be given in the next section. The only variables that were studied were the heating temperature and pressure.

The flow rate and temperature of feed stream in Aspen was set up as the same as the one used in WFD (and it is always a constant value). The flow rates of all the components from the distillate stream were chosen with the objective to be matched for both the two processes. An objective function (Equation 5.1) was derived for this system, which should be minimized for fitting experimental data with the model predictions. The weighting factor for each flow rate was reasonably assumed as 1 [104]. For each batch of separation in WFD, Aspen had the same temperature fixed, while pressure was adjusted iteratively. An optimum pressure under which the objective function reached to the lowest value was recorded as the final result for that batch.

The optimal fitting pressure was found out using the function “Sensitivity” in Aspen, which automatically calculates the distillation results for a series of different pressures. To determine which pressure is the most adequate, Equation 5.1 was inputted into Tabulate tab in Sensitivity module in Aspen.

$$FN = \sum_1^n C_i [(M_i - m_i) / m_i]^2 \quad (\text{Equation 5.1})$$

In this function (Equation 5.1), C_i is the weight factor, which equals to 1 for all the elements; M_i ($i=1, 2, \dots, n$) is the mass flow rate (lb/hr) of each component in distillate stream based on Aspen simulation result, while m_i ($i=1, 2, \dots, n$) is the mass flow rate (lb/hr) of each component in distillate stream from experimental WFD data. The sum of flow rate of distillate and residue were assumed equal to the flow rate of input stream. After calculation was finished in Aspen, pressure under which FN reached to the minimum value was recorded. Usually this pressure was lower than the running pressure in WFD.

5.3 Results and discussion

5.3.1 Affecting factors in WFD There are many factors that can affect the separation results in WFD, and these include flow rate, temperature and pressure of feed stream, temperature and pressure of column, rolling speed and blades number of wiper and cooling temperature of condenser. To examine the effect of these factors on the separation efficiency in WFD, we chose different conditions as the variables to run the experiment, and the consequent results are shown in this section.

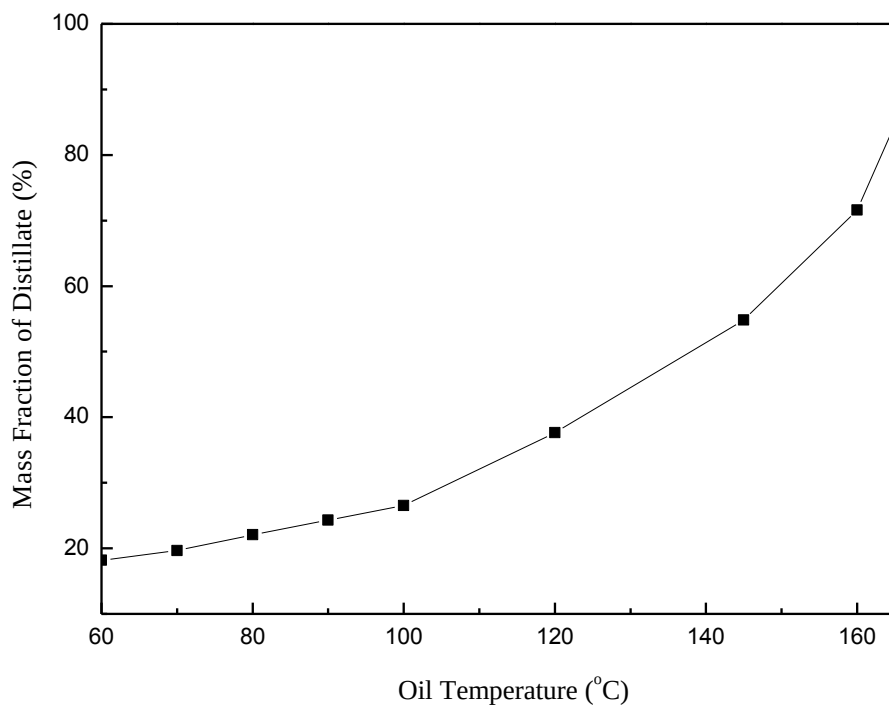


Figure 5.2 Effect of heating temperature on the ratio between distillate and feed using ozonolysis product with input flow rate of 3 ml/min and wiper rolling speed of 250 rpm, under still pressure of 2.7 kPa.

As shown in Figure 5.2, the mass fraction of distillate increased almost exponentially with the increase of heating temperature, which means the heating temperature can affect the separation results significantly. Composition of distillate also changed dramatically with the variation of heating temperature (from 60 to 160 °C) (Figure 5.3). At lower temperature, the main component in distillate was methyl hexanoate, followed by methyl nonanoate and dimethyl azelate, and this result was coincident with the order of boiling point of the three components; however, when heating temperature was increased, the mass fraction of dimethyl azelate in distillate started to increase gradually. After the temperature was above 120 °C, the main component in distillate was already dimethyl azelate. This increasing tendency was kept steadily in the following batches which were

operated under even higher temperature. This indicates that on one hand, higher temperature tends to increase the amount of distillate, but on the other hand it will also reduce the separation efficiency. In order to get a product with certain purity, the temperature must be chosen very carefully, and a tradeoff between the recovery and purity should be made based on the observation shown in Figure 5.3.

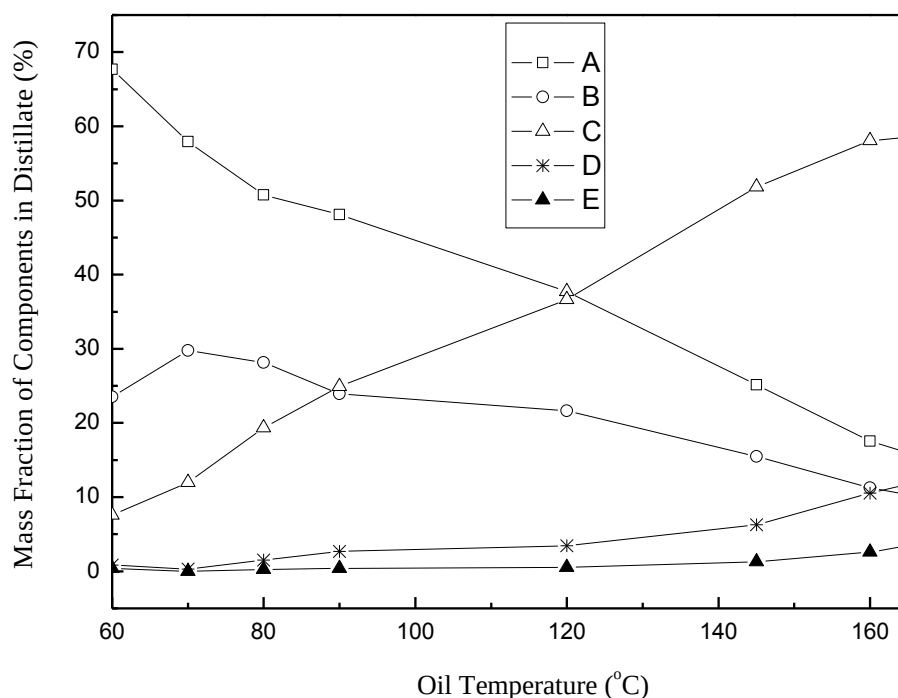


Figure 5.3 Effect of heating temperature on mass fraction of components using ozonolysis product with input flow rate of 3 ml/min and wiper rolling speed of 250 rpm, under still pressure of 2.7 kPa. A: Methyl hexanoate; B: Methyl nonanoate; C: Dimethyl azelate; D: Methyl palmitate; E: Methyl stearate.

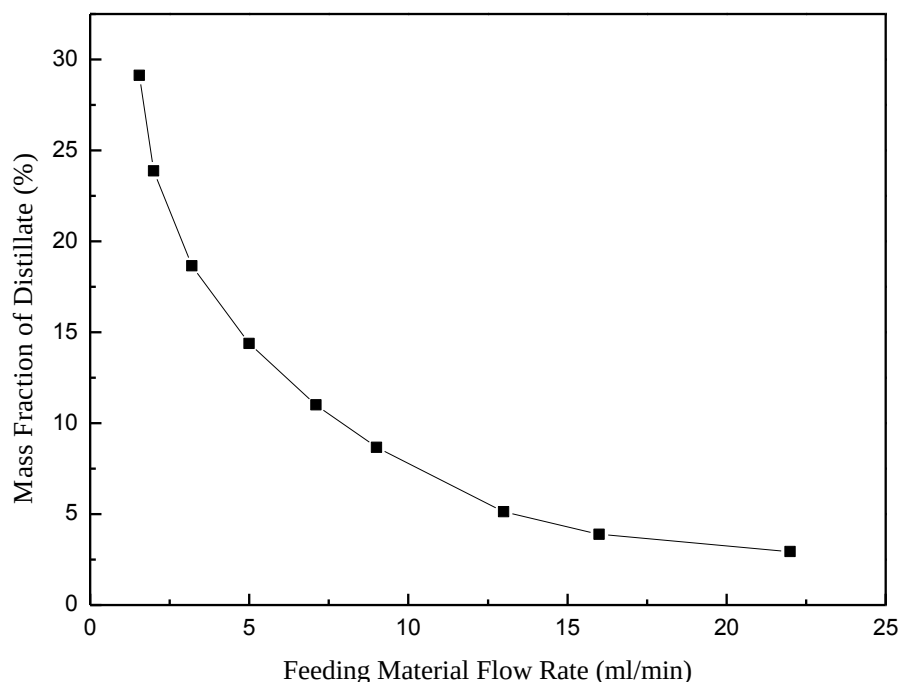


Figure 5.4 Effect of feed material flow rate on ratio of distillate to feed using ozonolysis product with wiper rolling speed of 250 rpm, heating temperature of 60 °C under pressure of 2.7 kPa.

Feed flow rate can also affect the separation substantially, especially in the range from 0 to 15 ml/min. With the feeding flow rate varying from 2 to 15 ml/min, the mass ratio of distillate to feed was decreased as much as 88% (Figure 5.3). This can be explained by the principle of heat exchange: consider the jacket wall as a small heat exchanger, in which the cold stream is the material needs to be separated and hot stream is the heating oil inside the wall, since the higher flow rate will decrease the heat transfer efficiency, the average temperature in the film turned to be lower than that with the lower flow rate, and this difference in temperature caused the difference in separation. In Figure 5.4, if the flow rate was arranged in the reversed order, the trend of the curve would be quite similar to that in Figure 5.2, which means, the infect of material flow rate is indeed an indirect

effect of the heating temperature. Based on the result displayed in Figure 5.4 and considering the productivity of the separation, we decided to choose 3 ml/min as the flow rate to run all the future experiments.

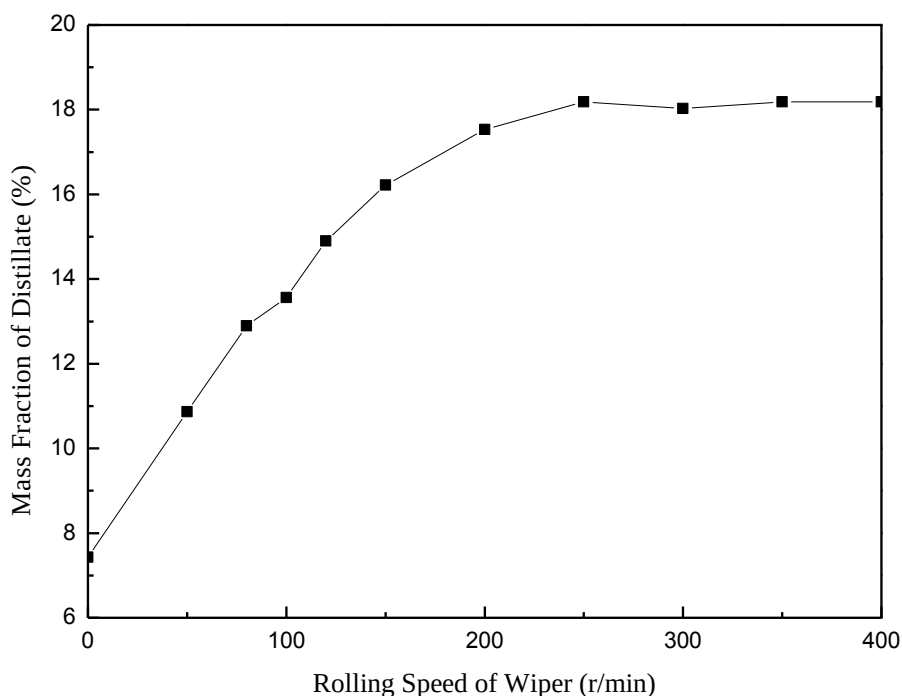


Figure 5.5 Effect of wiper rolling speed on ratio of distillate to feed using ozonolysis product with feed flow rate of 3 ml/min, heating temperature of 60 °C under pressure of 2.7 kPa.

Figure 5.5 demonstrated the impact of rolling speed of wiper on the separation result. The wiper spreads the material evenly on the heating area therefore to increase the heat transfer, and the faster it rolls, the more homogeneous the film is. The difference in rolling speed would also affect the average temperature of the liquid, and eventually affect the separation. It has been seen that with increase of rolling speed, the amount of distillate also increased, however after the speed reached to 250 rpm, the mass fraction of

distillate turned to be steady, so we chose 250 rpm as the rolling speed for all the batches of experiments.

There are also some other parameters which were not examined that can also affect the separation result, such as the flow rate of heating oil, the temperature of condenser, etc. In previous WFD study, some of these parameters have been investigated for the effect on heat transfer coefficient [101]. Since changing these parameters has to do with modifying the equipment, we will take them as fixed parameters in this project.

5.3.2 Vapor pressure data comparison and regression

Vapor liquid equilibrium data is the most important factor that can affect the simulation in Aspen. The databank of Aspen has vapor pressure data for all the compounds that we would use in this study except dimethyl azelate, which was estimated by molecular structure using UNIFAC functional groups in group contribution method. To guarantee the accuracy of the modeling, data obtained from experiment and Aspen databank was plotted in the same figure for comparison. According to Antoine equation, if $1/T$ was used as x axis, and $\ln P$ used as y axis, a linear relationship should be observed between the two. All of the experimental data was obtained from literatures in Reaxys website [105], and 300 to 500 K was chosen as the temperature range for this comparison, based on the availability of the data and the operation condition of regular WFD.

As displayed in Figure 5.6, vapor pressure data of methyl hexanoate (C7), methyl nonanoate (C10) and dimethyl azelate (C11) collected from Aspen fit the experimental data very well, if not considering a few deviated points. For methyl palmitate (C17) and methyl stearate (C19), not many experimental data points fell on the line, but on the

overall consideration, the fitting was still acceptable. So no regression was really needed for the five saturated methyl esters.

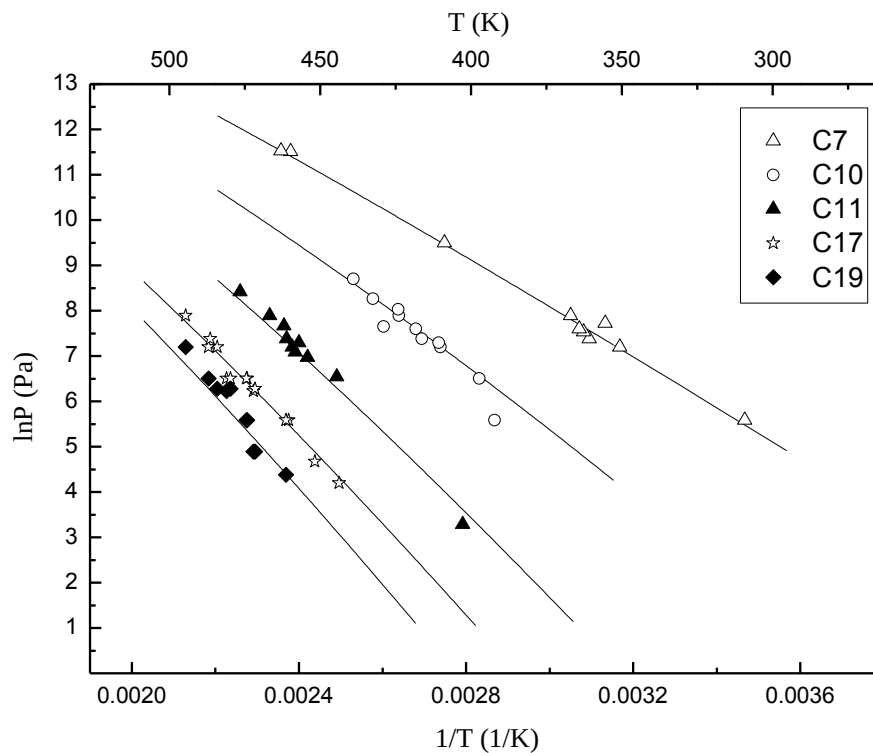


Figure 5.6 Comparison of vapor pressure for methyl esters from Aspen (continuous data) and literature (discrete points). C7: methyl hexanoate; C10: methyl nonanoate; C11: dimethyl azelate; C17: methyl palmitate; C19: methyl stearate.

The vapor pressure data curves for methyl oleate (C18:1) and methyl linolenate (C18:3) were very close to each other (Figure 5.7). They firstly kept a small distance from each other at lower temperature, and then joined together above temperature of about 500 K. The experimental data for C18:1 was a little bit higher than the data curve, which means C18:1 is more volatile in reality compared to the data in Aspen. However this difference is not obvious, therefore we also didn't make any change to the data in Aspen. The two

data points at about 640 K, which represent the vapor pressure for both of the two compounds under 1 atm, fitted very well.

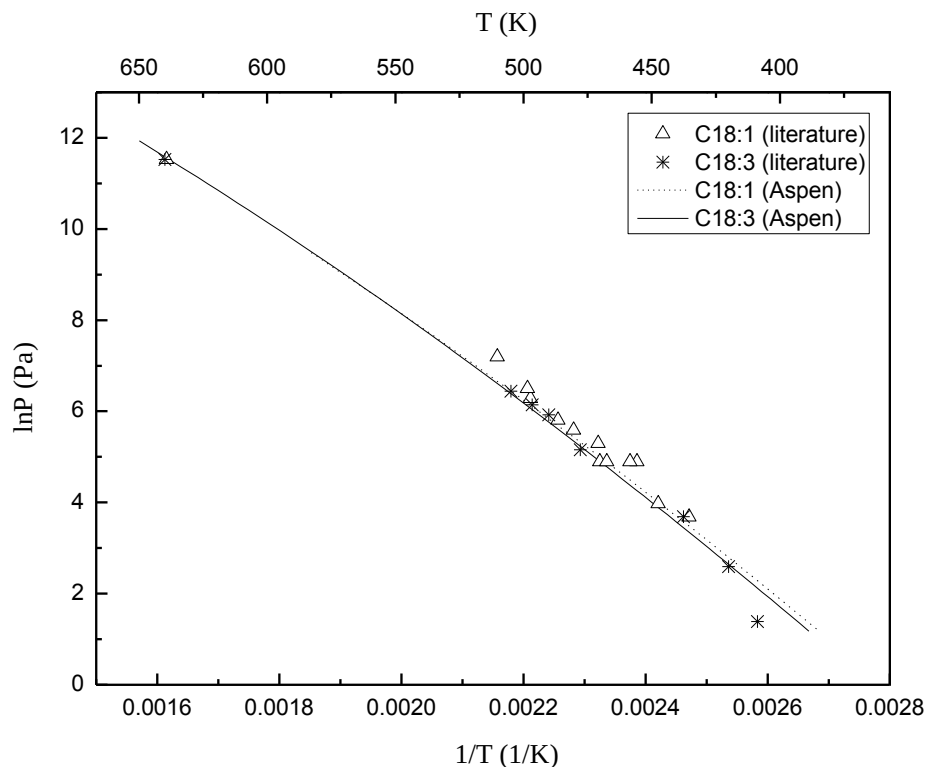


Figure 5.7 Comparison of vapor pressure data for unsaturated fatty acid methyl esters from Aspen and literature. (C18:1): methyl oleate; (C18:3): methyl linolenate.

The most apparent deviation from Aspen estimations was observed in the data for methyl linoleate (C18:2) (Figure 5.8). Regarding the original data curve obtained from Aspen, only the experimental data points near 510~530 K fell on it. Most of the experimental data showed an increasing trend along the temperature with a smaller slope than Aspen data. Using experimental data, the new parameters for Antoine equation were regressed and inputted into PLXANT parameter in Aspen. After this operation, the new vapor

pressure versus temperature curve was re-run, and the fitness was much better. New parameter was saved and used for the following simulation calculations.

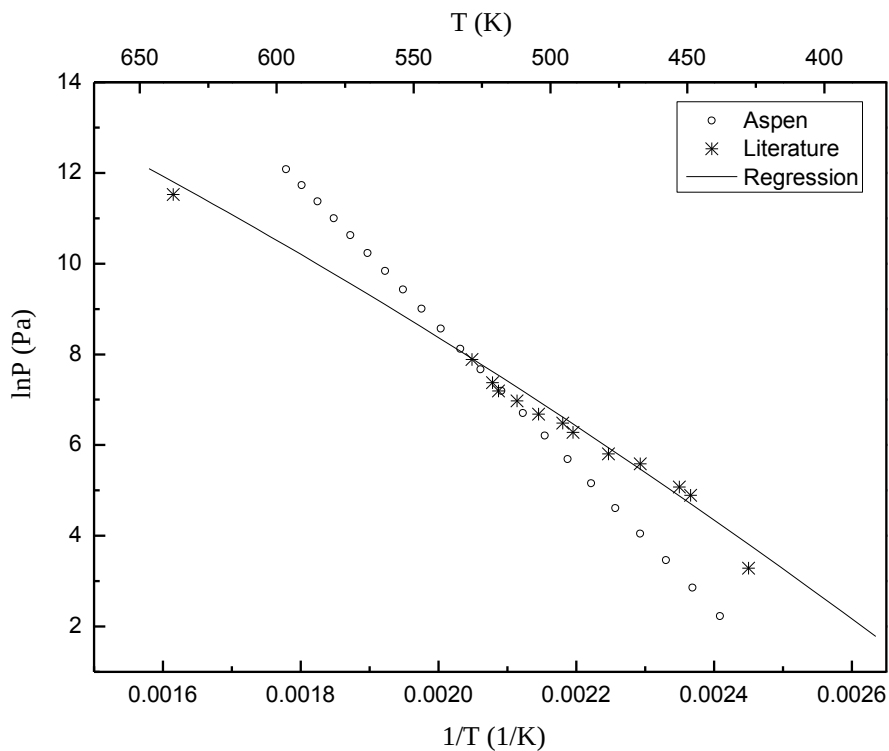


Figure 5.8 Comparison of vapor pressure data of methyl linoleate from Aspen (databank and after regression) and literature.

5.3.3 Simulation in Aspen for methanol and methyl hexanoate mixture

Two mixtures with different compositions of methanol and methyl hexanoate were separated using WFD, at temperature from 44 to 180 °C and constant pressure of 1atm. Simulation in Aspen Plus was conducted in the same condition as WFD including feed flow rate and operating temperature except pressure, thermodynamic method NRTL (all the binary interaction parameters were left empty) and ideal gas phase was chosen in project specification. Pressure was the only independent variable when running

Sensitivity in model analysis tools, and then the fitting pressure for each temperature was obtained by minimizing objective function (Equation 5.1). Under optimal pressure, it was found that the flow rates of distillate stream for both of the two components were very close to the experimental data as shown in Table 5.2.

Table 5.2 Modeling and experimental data comparison of component flow rates in distillate stream.

T (°C)	Component	Batch 1 ^[1]			Batch 2 ^[2]		
		Flow Rate of Distillate Stream (lb/hr)		Relative Error (%)	Flow Rate of Distillate Stream (lb/hr)		Relative Error (%)
		Aspen	Experiment		Aspen	Experiment	
44	M-hex	0.0279	0.0270	3.33	0.0238	0.0233	2.37
	Meth.	0.0758	0.0793	-4.41	0.1456	0.1509	-3.50
55	M-hex	0.0714	0.0729	-2.09	0.0491	0.0469	4.78
	Meth.	0.0881	0.0864	1.99	0.1606	0.1574	2.06
70	M-hex	0.0765	0.0761	0.45	0.0725	0.0723	0.25
	Meth.	0.0878	0.0908	-3.36	0.1657	0.1675	-1.09
80	M-hex	0.0952	0.0952	0.02	0.0892	0.0873	2.20
	Meth.	0.0896	0.0927	-3.35	0.1682	0.1785	-5.80
90	M-hex	0.1145	0.1140	0.44	0.0932	0.0900	3.50
	Meth.	0.0909	0.0948	-4.06	0.1683	0.1695	-0.74
100	M-hex	0.1480	0.1475	0.36	0.1040	0.1039	0.15
	Meth.	0.0929	0.0967	-3.95	0.1693	0.1714	-1.22
120	M-hex	0.1509	0.1531	-1.45	0.1254	0.1252	0.22
	Meth.	0.0926	0.0969	-4.44	0.1713	0.1720	-0.42
130	M-hex	0.1673	0.1652	1.28	0.1156	0.1148	0.70
	Meth.	0.0933	0.0986	-5.40	0.1699	0.1739	-2.27
150	M-hex	0.1848	0.1834	0.79	0.1314	0.1311	0.23
	Meth.	0.0939	0.1012	-7.21	0.1714	0.1762	-2.69
180	M-hex	0.2326	0.2366	-1.71	0.1574	0.1571	0.17
	Meth.	0.0957	0.0999	-4.18	0.1739	0.1783	-2.45

[1] Mass fraction of methyl hexanoate was 73%;

[2] Mass fraction of methyl hexanoate was 49%.

From Table 5.2 we can see that the simulation results obtained in Aspen fit the experimental data very well with a range of relative error from -7.2% to 4.78%, and more than 82% samples' relative errors are between -4.0 % and 4.0%.

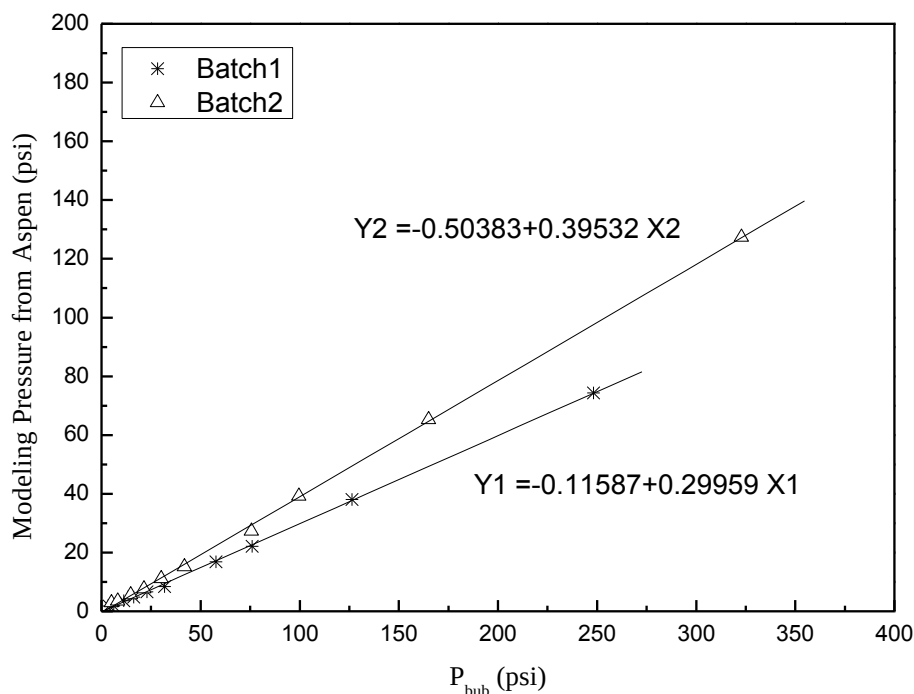


Figure 5.9 Bubble pressure of mixture versus modeling pressure from Aspen.

In Figure 5.9, the modeling pressures from Aspen were plotted as Y-axis and the bubble pressures of the mixture at the temperature of heating temperature were plotted as X-axis, and as shown in the figure, the two pressures form a linear correlation. The slope of the fitting line for batch 2 is higher than that for batch 1. This may be because the effective pressure correlates with the distillate fraction, and higher distillate fraction will have a higher effective pressure, so the more volatile mixture will have a higher effective pressure. The sample mixture of batch 2 contains higher mass fraction of methanol, it is therefore more volatile than batch 1 and led to a larger slope of the fitting line.

5.3.4 Simulation in Aspen for ozonolysis product mixture

A mixture prepared by ozonolysis and Oxone oxidation containing 5 methyl esters, methanol and water was separated using WFD. Most of the compounds in this sample

could be identified and quantified, with only 11.2% (mass fraction) as unknown impurity. Impurity components were defined as one PSEUDO component which was assumed having the same properties as methyl stearate. Feed flow rate was 3 ml/min (0.3801 lb/hr), condenser temperature was 3 °C, and the rolling speed of wiper was 250 rpm. For each batch under different temperature, operation was repeated for 3 times, and the average flow rate for each component was eventually applied. UNIFAC was chosen as thermodynamic method, and missing parameters were estimated by Aspen based on the chemical structures of components. Figure 5.10 shows a satisfactory qualitative agreement of the results obtained from Aspen and experimental operation. The biggest error rate did not exceed 10%. Inconformity in fitting may be caused by approximation of the impurity and estimation of properties of some compounds.

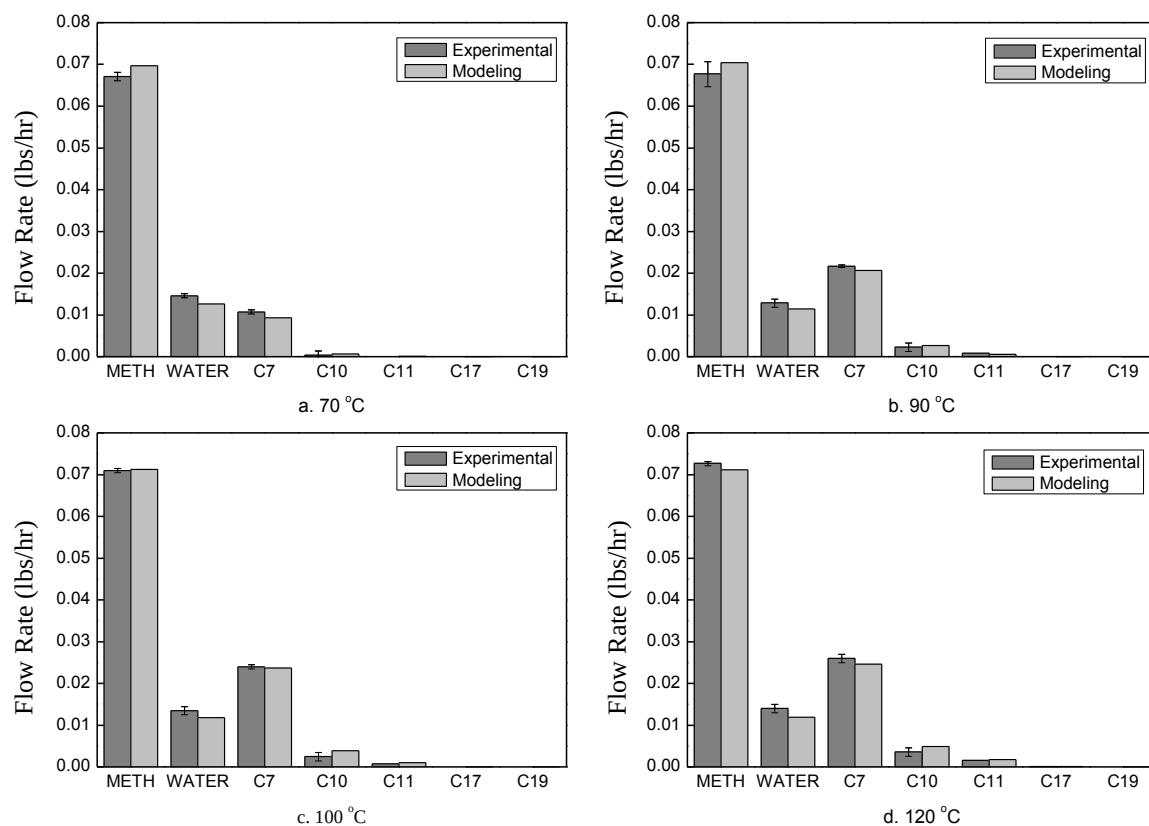


Figure 5.10 Comparison of component flow rate in distillate for experimental and modeling data of saturated methyl ester mixture. METH: Methanol; C7: Methyl hexanoate; C10: Methyl nonanoate; C11: Dimethyl azelate; C17: Methyl palmitate; C19: Methyl stearate.

As demonstrated in Figure 5.11, it still holds true for this multi-component system that the modeling pressure in Aspen is linear related to the bubble pressure of the mixture, however, the intercept for the fitting line is much higher than the two-component system and the slope is much lower.

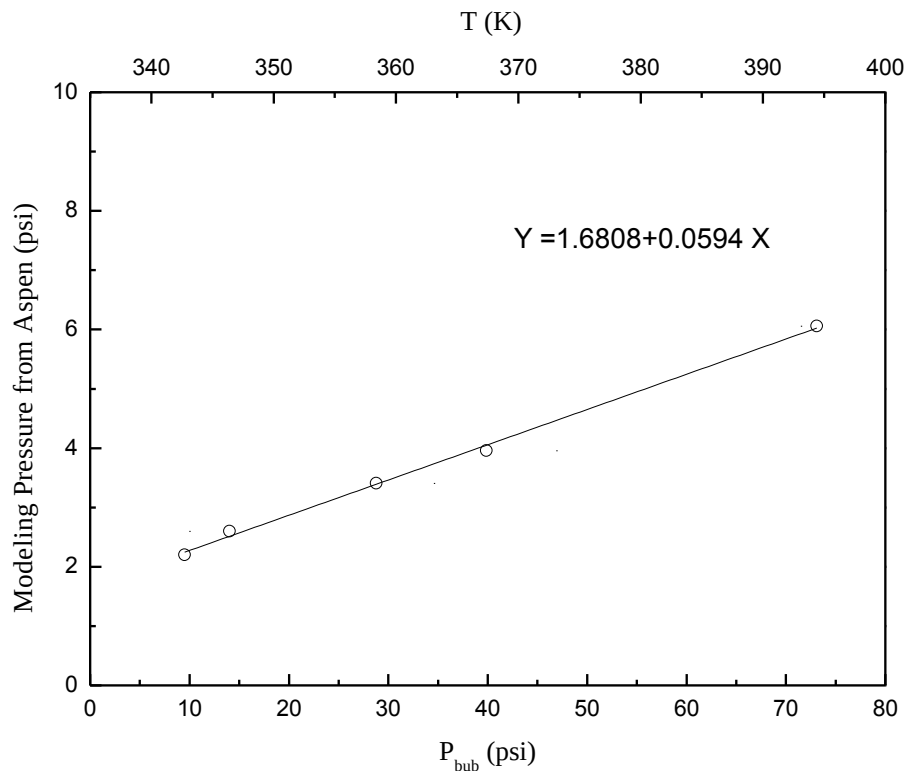


Figure 5.11 Bubble pressure of mixture versus modeling pressure in Aspen for products prepared through ozonolysis. Operating pressure was 1 atm, feed flow rate was 3 ml/min, condenser temperature was 3 °C, and the rolling speed of wiper was 250 rpm.

5.3.5 Simulation in Aspen for FAMES mixture

In previous discussion, we have explored the linear correlation between the bubble pressure of the mixture at heating temperature and the modeling pressure from Aspen while separating under the same temperature and the operating pressure in WFD was fixed at 1 atm. In this section, we would like to study on the relationship between the modeling pressure and operating pressure while the heating temperature of WFD is fixed. A mixture consisting of five fatty acid methyl esters (FAMES) was used to study the equilibrium simulation in Aspen for WFD. Similar to the saturated ester mixture, 5.33%

of mass fraction of the sample was impurity, and was defined as one PSEUDO component, assumed with the same properties of methyl linolenate. Volumetric feed flow rate was also 3 ml/min, condenser temperature was 3 °C, and the rolling speed of wiper was 250 rpm. This time the heating temperature was fixed at 170 °C, and operating pressure was varied from 0.493 psi to 7.802 psi. Thermodynamic activity coefficient model was UNIFAC, and by evaluating the structures of the components the missing parameters were estimated through group contribution method.

By fitting the distillation results from WFD into Aspen, the optimal pressure of flash separator in response to each operating pressure of WFD was calculated. A satisfactory qualitative agreement between the experimental data and Aspen simulation result was shown in Figure 5.12. Relative error fell in to the range of -10% to 10%.

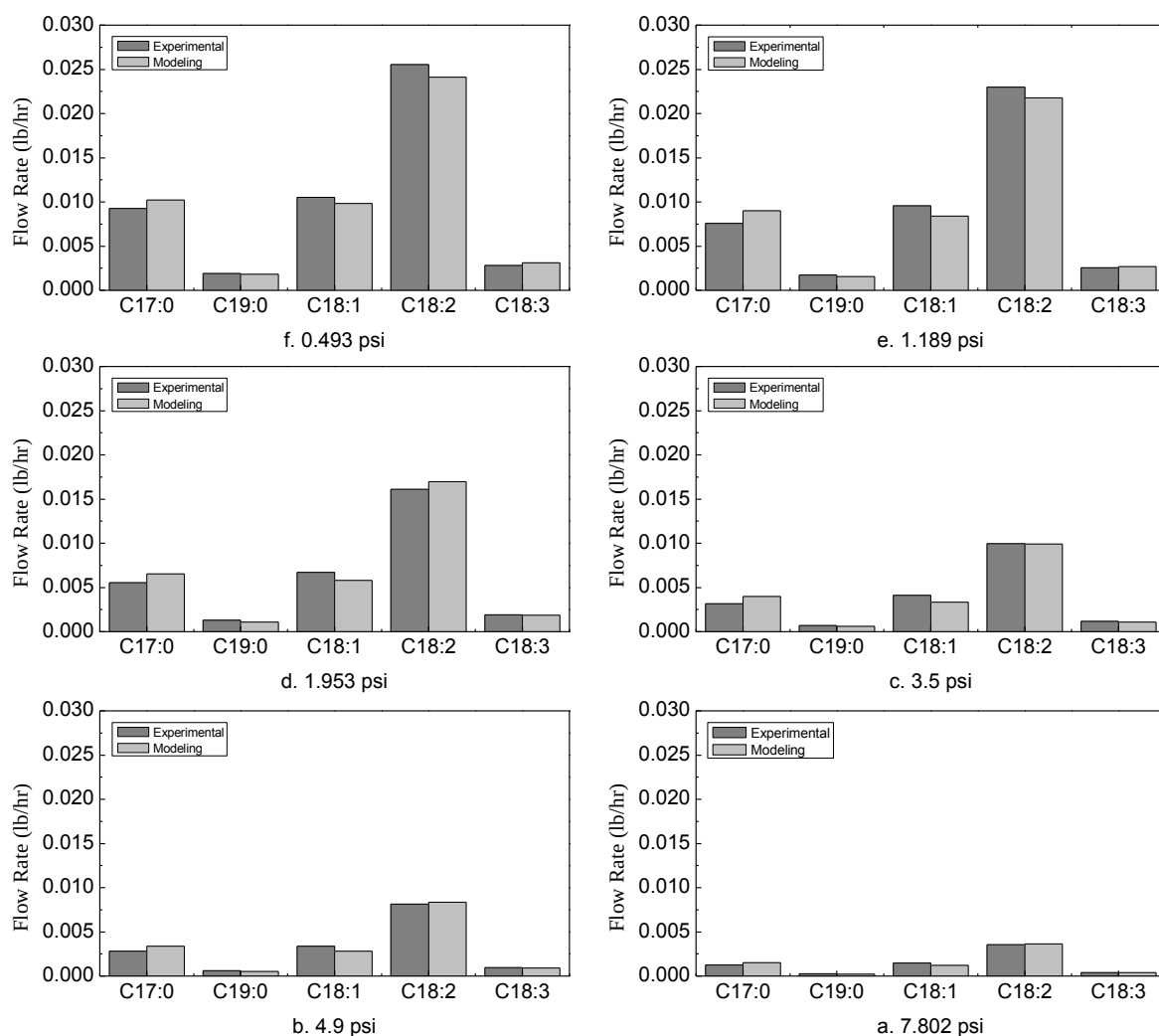


Figure 5.12 Experimental and modeling data comparison of component flow rate in distillate for separation of FAMES. C17:0: Methyl palmitate; C19:0: Methyl stearate; C18:1: Methyl oleate; C18:2: Methyl linoleate; C18:3: Methyl linolenate.

The dependence of component distillate flow rate on operating pressure was obviously indicated in Figure 5.13. As indicated by the data, operation pressure was much higher than the simulation pressure in Aspen when operating pressure was higher than about 0.2 psi. The modeling pressure in Aspen increases exponentially with the increase of operating pressure of WFD. In fact, the actual operating temperature in WFD column is

lower than the heating temperature, which is to say, the real temperature in WFD system is lower than in Aspen. Even under this circumstance, to gain the same separation result in the flash separator in Aspen it still needs higher vacuum than in WFD.

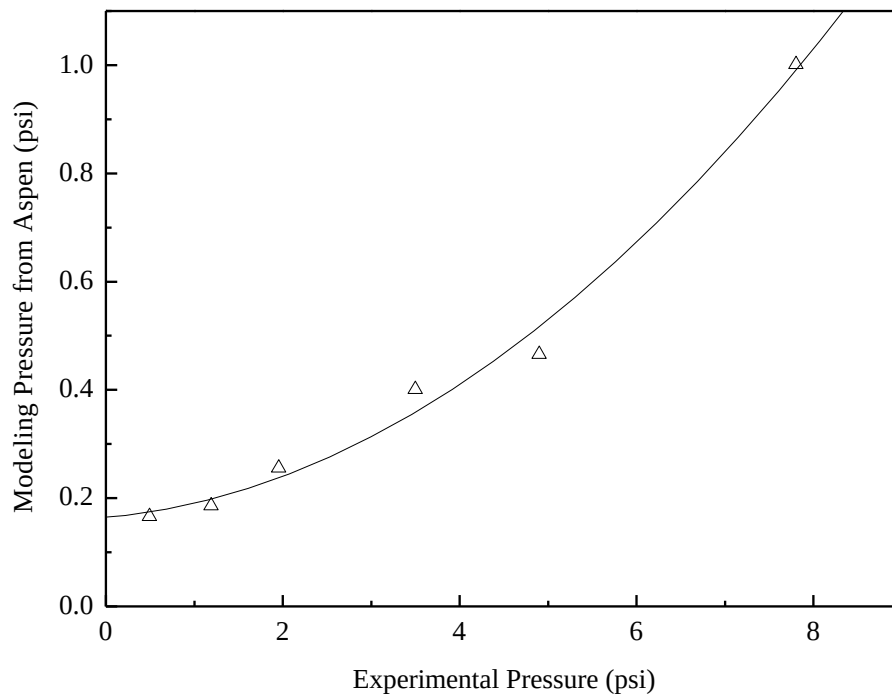


Figure 5.13 Experimental pressure of WFD versus modeling pressure in Aspen for FAMEs. Operating temperature was 170 °C, feed flow rate was 3 ml/min, condenser temperature was 3 °C, and the rolling speed of wiper was 250 rpm.

5.4 Conclusion

Equilibrium simulation of WFD using one stage flash separation process in Aspen was developed and evaluated. Feed flow rate and heating temperature for WFD were adopted by flash separation, and only operating pressure was calculated. The optimum pressure for flash separator that generates the similar separation results was found out by using Sensitivity module in Aspen and minimizing the objective function defined in Tabulate

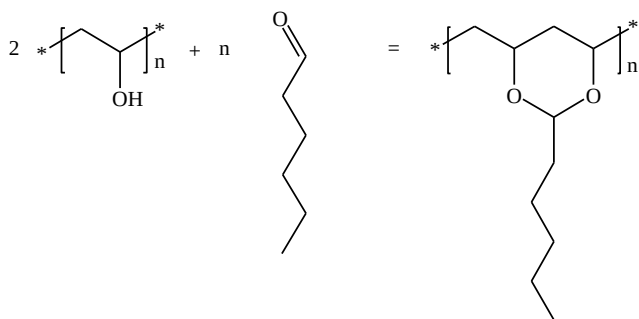
tab. Three different mixtures (methanol and methyl hexanoate, products of ozonolysis in methanol and FAMEs mixture) were used to verify this modeling method, and different operating conditions including temperature and pressure were applied to conduct experiments. For all of the mixtures above, satisfactory quantitative agreement was obtained between experimental and modeling result.

When operating pressure in WFD is fixed, the study showed that modeling pressure in Aspen was proportional to the pseudo bubble pressure of the mixture at the heating temperature of WFD, and the slope of the fitting straight line is higher for more volatile mixture. When operating pressure of WFD increases, the modeling pressure from Aspen also increases in a higher speed. For FAMEs mixture, it was found that when operating pressure in WFD was higher than certain value (e. g. 0.2 psi), to have the same separation result the required pressure in flash separator in Aspen was higher than that in WFD. This study may contribute to the equilibrium simulation of WFD in the future, and in order to simulate WFD without depending on preliminary data, further study on the relationship between operating pressure in WFD and modeling pressure in Aspen is needed. For example, more experiments using materials with different components and compositions should be conducted; also more experiments using the same material under different operating pressures should be carried out in order to examine the relationship between operating pressure in WFD and modeling pressure in Aspen.

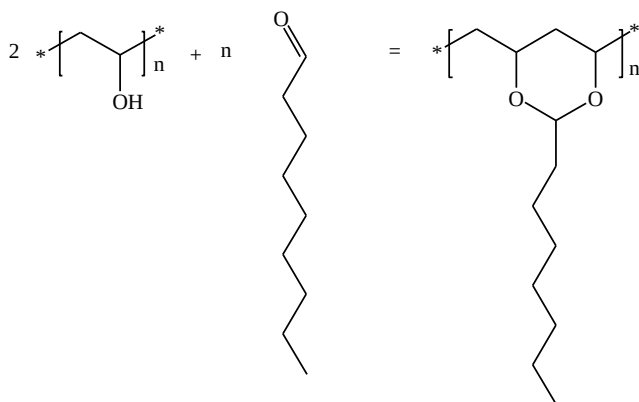
Chapter 6: Polyvinyl Acetal Synthesis and Characterization

6.1 Introduction

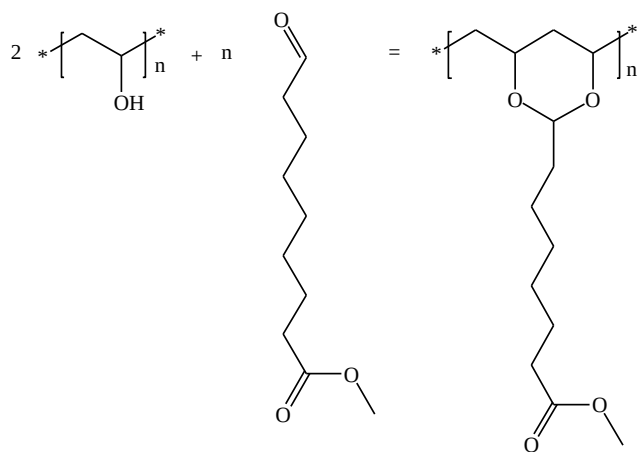
Polyvinyl acetal polymer (poly-(vinyl acetal)) is usually formed by the reaction of aldehydes with polyvinyl alcohol (PVOH). During the reaction, adjacent alcohol groups from PVOH react with one molecule of aldehyde and form an acetal ring. When the aldehyde participating in the reaction is hexanal, nonanal or 9-oxononanoate, the consequential polymer will be polyvinyl hexanal (PVH), polyvinyl nonanal (PVN) or polyvinyl 9-oxononanoate (PVON), which will be the subject of the study in this chapter. The reactions for the three aldehydes with PVOH respectively are shown in Figure 6.1:



(A) Reaction for polyvinyl hexanal



(B) Reaction for polyvinyl nonanal



(C) Reaction for polyvinyl 9-oxononanoate

Figure 6.1 Reactions for polyvinyl acetal polymer preparation.

PVOH is a crystalline thermoplastic material which is highly polar and resistant to hydrocarbons and hard to dissolve in almost any solvent except water. The solubility of

PVOH in water depends on the degree of hydrolysis and molecular weight [106]. Completely hydrolyzed PVOH are soluble only in hot water whereas partially hydrolyzed grades (88 mol%) are soluble at room temperature [107]. In industry, PVOH is used to make water-soluble films for packaging, barrier layers in multi-layer co-extrusions and blow moulding containers [108].

In the group of polyvinyl acetal polymers, the most widely used material is polyvinyl butyral (PVB), which is formed by reaction of butyraldehyde with PVOH. PVB is an amorphous material which can be used as a safety glass interlayer such as windshield for vehicles. PVB has this application is due to its high strength, low density, water resistance, transparency and stickiness to glass. It is also used in adhesives and coatings [109].

Preparation methods of polyvinyl acetal can be found in several patents[110], and most methods include addition of acid catalyst such as hydrochloric acid, sulfuric acid, solid acid, etc. In 1954, a patent from DuPont claimed a continuous process to prepare polyvinyl acetal in a strong acid aqueous solution (pH 1.5 to 2.5) under 60-100 °C and obtained 69-75% acetalized polyvinyl acetal product [111]. After two years, the above method was modified by DuPont, in which the reaction of PVOH and aldehyde was conducted in aqueous solution with the presence of a plasticizer under temperature of 20-65 °C for 10-100 mins, and afterwards the slurry with product was formed [112]. In 2004, a Japanese patent application introduced a method of acetalizing PVOH in aqueous solution with a solid acid as catalyst with application of high pressure (8 MPa) under 100 °C for 30 mins, the polymerization degree of polyvinyl acetal product was reported as 500 [113].

Another method published by Fitzhugh et al.[114] demonstrated the reaction of PVOH with aldehyde in a mixture of solvents containing both ethanol and 1, 4-dioxane (mass ratio 1:1) with sulfuric acid as catalyst under 80 °C for 9 hrs. After this reaction, the product was precipitated by washing with water. Since polyvinyl acetal dissolves well in this solvent, a higher degree of acetalization can be achieved compared to the aqueous solution process. The disadvantages of this process are the long reaction time and high cost, and thus it is less feasible for industrial production.

The preparation of PVH can be carried out through all the above mentioned methods, however, considering the equipment availability and the economic due to usage of expensive solvents that are not easily recoverable al feasibility of the process we will only evaluate two methods in this chapter. Three aldehydes (hexanal, nonanal and 9-oxononanoate) obtained from ozonolysis of soybean FAMES were chosen to react with PVOH, and the resulting products were characterized and compared among each other as well as with PVB, a commercial polyvinyl acetal. The properties examined include decomposition temperature, glass transition and melting temperatures, molecular weight and degree of acetalization.

6.2 Experiments

6.2.1 Materials

Hexanal ($\geq 99\%$), nonanal ($\geq 95\%$) and 1, 4-dioxane ($\geq 99\%$) were purchased from Sigma-Aldrich; 200 proof ethanol was purchased from KOPTEC; PVOH (hydroxylation degree of 99 mol%) and polyvinyl butyral (PVB) were provided by Kuraray America Inc. In some reactions, hexanal (95%), nonanal (93%) and 9-oxononanoate (88%) were obtained from ozonolysis product purified through lab-scale fractional distillation.

6.2.2 Preparation of PVOH solution

Aqueous solution of PVOH with concentration of 5 wt% was prepared using the following method: 50 g of PVOH were added slowly into 900 g of cold water (15-25 °C) with continuous stirring. At the same time, the slurry was heated until temperature reached 97- 98 °C. If PVOH was completely dissolved at this time, 50 g of hot water was added and the preparation was completed. If not, stirring at this temperature was continued and hot steam was passed through the slurry. The amount of steam should be recorded and should not exceed 50 g. After PVOH is completely dissolved, the missing amount of water between 50 g and the mass of injected steam was added.

6.2.3 Preparation of polyvinyl acetal in aqueous solution

Take 200 g of 5% PVOH aqueous solution, add 15 g of hexanal (or 21.3 g of nonanal or corresponding weight of material based on 2:1 molar ratio between PVOH and aldehyde) and 2 g of sulfuric acid, heat up the mixture and keep the reaction run at the temperature of 75-80 °C with mechanical agitation and reflux for 30 mins to 1 hr.

Upon completion of the reaction, polyvinyl acetal will congeal to white lumps and float on top of the solvent. Filter out the polymer using a Buchner funnel and wash the product with 100 g of water (to remove PVOH) and 100 g of methanol (to remove aldehyde) successively. Cut the lumps of polymer into small pieces and wash with water and methanol one more time, and then put product into oven with temperature maintained at 50-60 °C for 24 hrs to dry out.

6.2.4 Preparation of polyvinyl hexanal in organic solution

Add 10 g of PVOH to 275 g of 1, 4- dioxane and ethanol mixture (weight ratio 1:1) and preheat the mixture to 70 °C for 1 hr with stirring and then add 15 g of hexanal (or the same molar amount of other aldehydes) and 2 g of sulfuric acid into this mixture. Increase the temperature to 75 - 85 °C with mechanical agitation at a speed of 1800 rpm under reflux.

Keep the reaction run for more than 5 hrs with the same temperature and agitation speed maintained. Upon the completion of reaction, add water into reactor to precipitate the polyvinyl acetal resin under continuous stirring, and then wash the product with 100 g of water (to remove PVOH) and 100 g of ethanol (to remove aldehyde and 1, 4-dioxane) successively. Keep the resin in 5% of KOH solution for 4.5 hrs to stabilize the polymer. After stabilization, wash the product with water and cut the lumps of polymer into small pieces, wash with water one more time and then put the product in oven at 50-60 °C for 24 hrs for drying.

6.2.5 Thermogravimetric analysis (TGA)

TGA was conducted with a TA Instruments Model TGA Q50 machine (New Castle, DE). The sample was weighted between 5 and 15 mg and placed into an aluminum pan inside a platinum pan to avoid contamination. The sample was firstly heated up to 550 °C at a rate of 10 °C/min with the supply of nitrogen, and when the temperature reached to 550, a homothermal mode with a time period of 20 mins was applied and the gas was switched from nitrogen to air to burn the materials completely. Since the material only contains

carbon, hydrogen and oxygen molecules, no residue was left in the pan and the final weight reduced to 0.

6.2.6 Differential scanning calorimetry (DSC)

DSC analysis was carried out in a TA Instruments Model DSC Q20 machine (New Castle, DE). The sample was weighted between 5 and 10 mg and placed into an aluminum pan with a compatible lid. The sample was first heated up to 220 or 300 °C at a rate of 20 °C/min and then cooled down to -50 or -80 °C at a rate of 10 °C/min. Starting at the lowest temperature, the sample was heated up 220 or 300 °C again with 10 °C/min. The data from last run from -80 or -50 °C to 220 or 300 °C was chosen to be plotted in the final result figure.

6.2.7 Gel permeation chromatography (GPC) for molecular weight measurement

Average molar mass of polyvinyl acetals from different reaction was determined by gel permeation chromatography (GPC) equipped with a refractive index detector (Shimadzu, Tokyo, Japan, RID-10A) and a combination of three columns (Waters Co., Israel). Tetrahydrofuran was applied as mobile phase and the flow rate was set at 0.50 mL/min at 40 °C. Polystyrene was used as standard to obtain the calibration curve for average molar mass calculation.

6.2.8 ¹H NMR analysis

¹H NMR was conducted on a Unity Plus 500 MHz NMR spectrometer from Varian Inc. (Palo Alto, CA, USA) to determine the acetalization degree of polyvinyl acetals. A

sample was dissolved in CDCl_3 and the spectrum was recorded using the solvent peak as the internal standard.

6.3 Results and Discussion

6.3.1 Thermogravimetric analysis (TGA)

TGA was conducted with a TA Instruments Model TGA Q50 machine (New Castle, DE). The sample was weighted between 5 and 15 mg and placed into an aluminum pan inside a platinum pan to avoid contamination. The sample was firstly heated up to 550 °C at a rate of 10 °C/min with the supply of nitrogen, and when the temperature reached to 550, a homothermal mode with a time period of 20 mins was applied and the gas was switched from nitrogen to air to burn the materials completely. Since the material only contains carbon, hydrogen and oxygen molecules, no residue was left in the pan and the final weight reduced to 0.

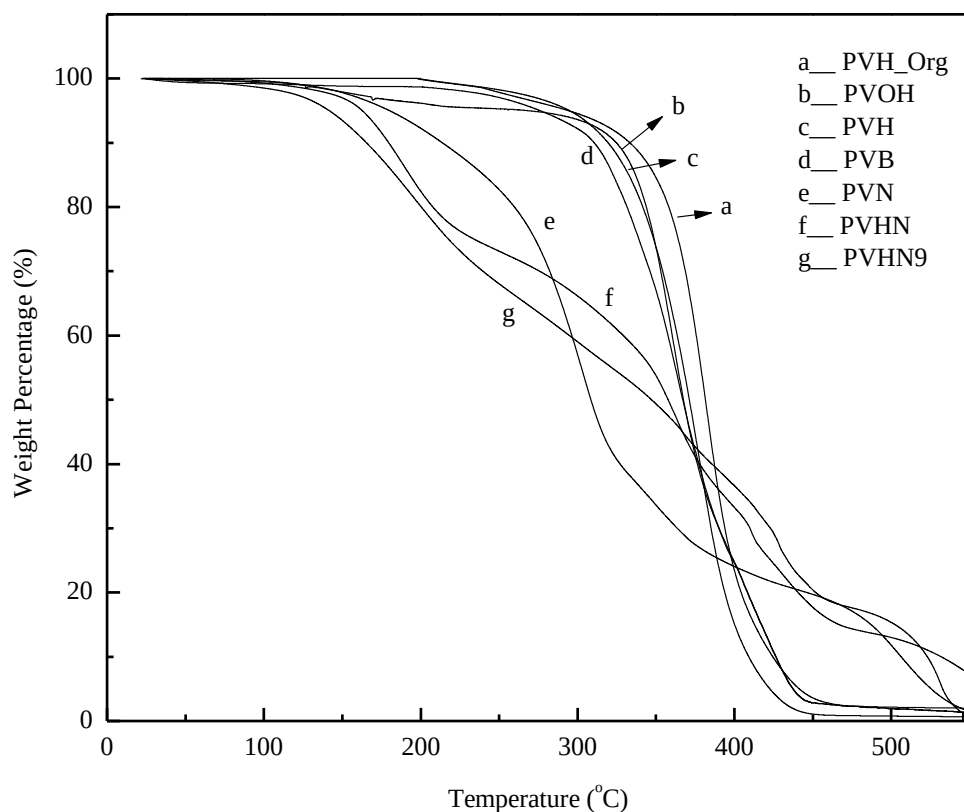


Figure 6.2 TGA weight percentage change with temperature profiles of polyvinyl alcohol and acetal polymers.

PVOH: polyvinyl alcohol provided by Kuraray; PVB: polyvinyl butyral provided by Kuraray; PVH: polyvinyl alcohol reacted with hexanal based on stoichiometry in water; PVH_Org: polyvinyl alcohol reacted with hexanal based on stoichiometry in organic solvent; PVN: polyvinyl alcohol reacted with nonanal based on stoichiometry; PVHN: polyvinyl alcohol reacted with hexanal and nonanal (molar ratio 1:1) based on stoichiometry; PVHN9: polyvinyl alcohol reacted with hexanal, nonanal and methyl 9-oxononanoate (molar ratio of the three aldehydes: 1:1:1).

To determine the potential of the various aldehydes produced by ozonolysis of FAMES for polymer application, various polymers were synthesized using different solvent

systems (aqueous and organic) and different aldehyde combinations with PVOH. The various polymers produced were initially tested for their thermal stability using thermogravimetric analysis (TGA) and compared to the commercially available PVB and PVOH as controls. The weight percentage change as a function of temperature for 6 different polyvinyl polymers and PVOH were plotted in Figure 6.2. It was observed that the weight loss of PVHN9 started at the lowest temperature ($< 100\text{ }^{\circ}\text{C}$) among the polymers tested herein, while PVHN showed the second lowest initial degradation temperature, at around $140\text{ }^{\circ}\text{C}$. PVN followed as the third compound that started decomposing, at a similar temperature as PVHN, showing a lower initial drop in weight, followed by a larger drop after $270\text{ }^{\circ}\text{C}$ and a third instant drop at around $500\text{ }^{\circ}\text{C}$. The initial decomposition temperatures for PVH (organic solvent), PVOH, PVH and PVB are much higher than PVN, PVHN and PVHN9, which generally start around $230\text{ }^{\circ}\text{C}$. Comparing the structure of the two groups of compounds, the differences reside in that the side chains of former group of compounds are shorter than that of the latter group of compounds. In addition, the latter group of compounds like PVHN and PVHN9 contain more than one type of acetal side chains, which may also reduce the thermal stability of the polymer and increase the number of decomposition stages as a function of temperature due to their heterogeneity.

The decomposition temperatures of PVH and PVOH are very similar, at about $375\text{ }^{\circ}\text{C}$, and both are slightly higher than PVB. However, PVH made in organic solvent has an observably higher decomposition temperature, at around $380\text{-}390\text{ }^{\circ}\text{C}$. This difference may be explained by the fact that the polymer was made in organic solvent, and unlike the aqueous solvent system, the product was completely dissolved during the process. The

polymerization in homogeneous systems allows the reaction to occur in a larger extent, creating a larger number of acetal side chains bound to the PVOH backbone. Usually, more side chains homogeneously distributed should provide higher thermal stability and this explains why the PVH made in organic solvent is more stable than the PVH made in aqueous solvent. As PVH was the polymer that showed the highest thermal stability among the various polymers tested in this study, including the commercial PVB, we focused our study in the characterization of PVH.

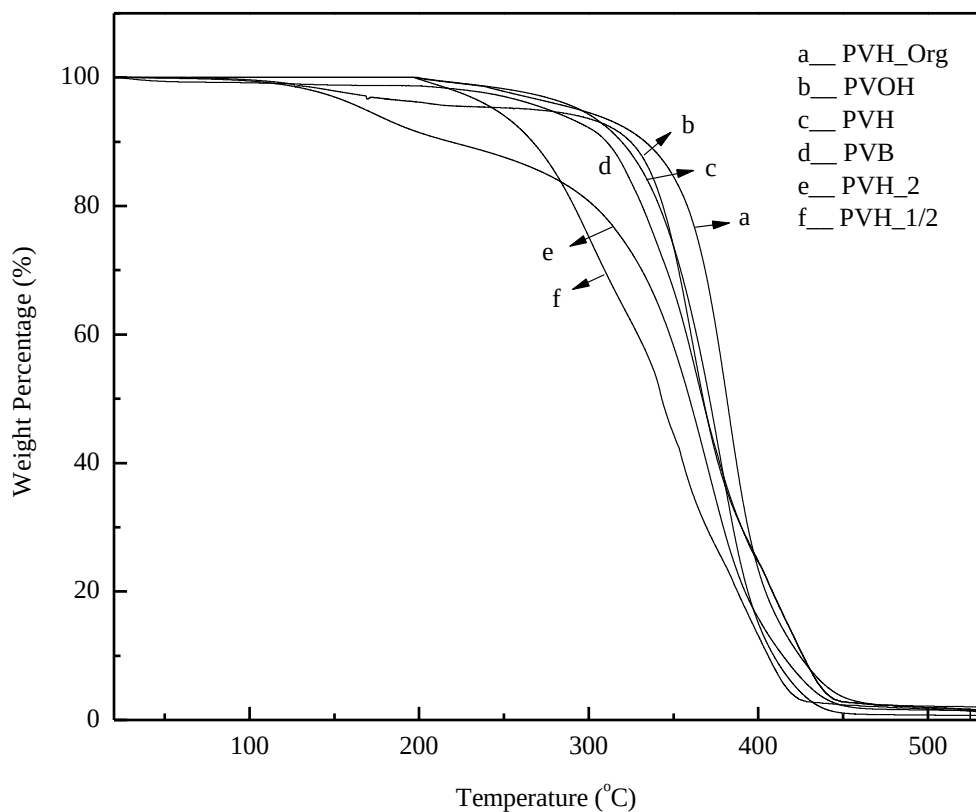


Figure 6.3 TGA weight percentage change with temperature profiles of polyvinyl alcohol and acetal polymers.

PVOH: polyvinyl alcohol provided by Kuraray; PVB: polyvinyl butyral provided by Kuraray; PVH: polyvinyl alcohol reacted with hexanal based on stoichiometry in water;

PVH_Org: polyvinyl alcohol reacted with hexanal based on stoichiometry in organic solvent; PVH_2: polyvinyl alcohol reacted with hexanal with 2 times of stoichiometric amount of hexanal; PVH_1/2: polyvinyl alcohol reacted with hexanal with 0.5 times of stoichiometric amount of hexanal.

To determine potential changes in thermal stability due to addition of hexanal in different proportions to the reaction with PVOH, the polymer was synthesized with in water with a stoichiometric ratio of hexanal to PVOH (PVH), with double the stoichiometric ratio of hexanal to PVOH (PVH_2) and half the stoichiometric ratio of hexanal to PVOH (PVH_1/2). TGA for the different polymers was obtained and compared with controls such as PVOH, PVB and PVH produced in organic solvent (Figure 6.3). The results show that the PVH_2 started decomposing at lower temperatures, around 130 °C, which coincides with the boiling point of hexanal. This suggests that unreacted hexanal trapped into the polymer matrix, which could not be washed out, is evaporating from the sample and is responsible for the initial weigh loss for PVH_2. If we would not take into account this initial weight loss due to solvent evaporation, the thermal stability of the polymer would be similar to the one showed by PVB. In the case of PVH_1/2, the weight loss profile shows an early decomposition temperature of about 200 °C, presenting a lower slope compared to the controls. This observation suggests that the polymer is more heterogeneous in terms of its building block units, which may also contribute to the lower thermal stability of the product.

From the results of this experiment, it is clear that PVH produced using a stoichiometric ratio of hexanal to PVOH shows better thermal stability than using lower hexanal to PVOH ratios. Also, addition of higher hexanal content to the reaction mixture did not

show any improvements in the thermal stability of the product and may create processing issues in the future for removal of excess hexanal from the polymer matrix. Therefore, for industrial production of PVH, the synthesis protocol using a stoichiometric ratio of hexanal to PVOH is highly recommended in case of using water as solvent system.

6.3.2 Differential scanning calorimetry (DSC)

To evaluate the glass transition and melting temperatures of PVH produced using various ratios of hexanal to PVOH in water, a DSC analysis was performed. Figure 6.4 shows the DSC results of PVH produced using different hexanal-to-PVOH ratios and the respective controls, notably PVOH and PVB. The results show that PVOH has a glass transition temperature (T_g) of 85 °C and melting temperature (T_m) of 230 °C. A clear T_g of PVB shows up between 65-70 °C which is identical to the reported value provided by Kuraray Inc. [115]. The T_g of PVH and PVH_2 appears at a temperature between 30 and 40 °C which is lower than that of PVB. This indicates that longer side chains of polyvinyl acetals may contribute to lowering the T_g of polyvinyl acetal polymers. The T_g of PVH_1/2 could be clearly determined by the DSC plot, which may have to do with the high level of heterogeneity of this polymer. Unlike PVOH, all the polyvinyl acetals do not show a melting point within the range of temperatures analyzed in this study.

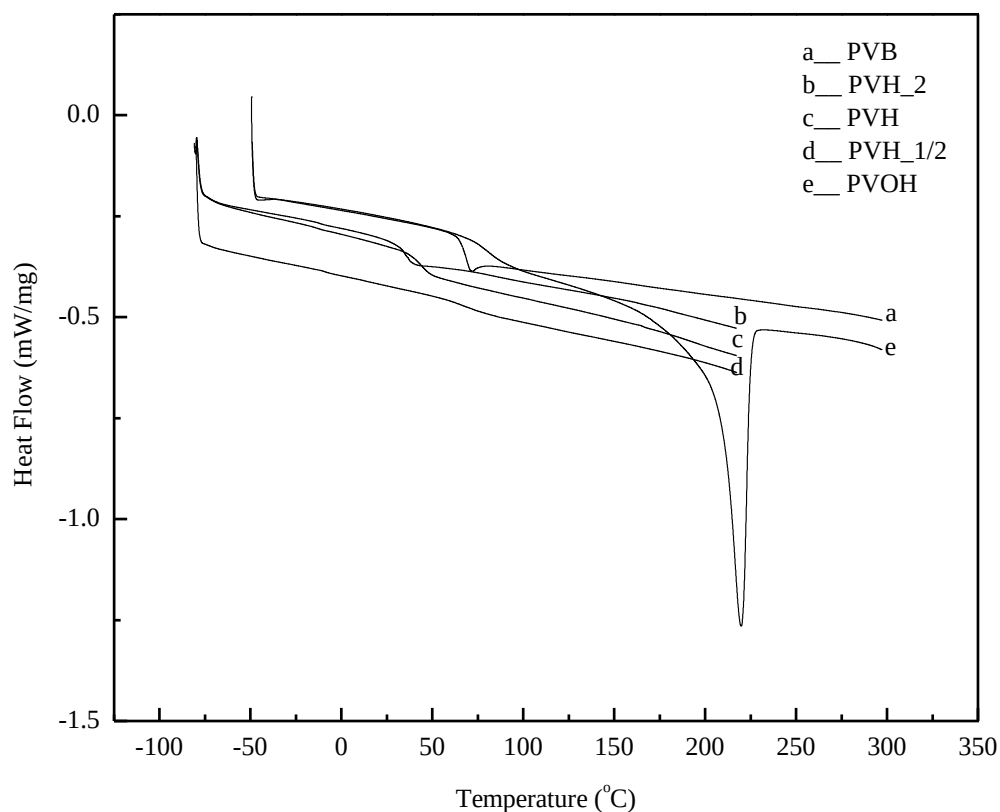


Figure 6.4 DSC spectra of polyvinyl acetals. PVB: polyvinyl butyral provided by Kuraray; PVOH: polyvinyl alcohol provided by Kuraray; PVH: polyvinyl alcohol reacted with hexanal based on stoichiometry; PVH₂: polyvinyl alcohol reacted with 100% excess hexanal based on stoichiometry; PVH_{1/2}: polyvinyl alcohol reacted with half amount of hexanal based on stoichiometry.

Comparing the DSC results obtained for PVH with the other polyvinyl acetals that are possible to produce from products of FAME ozonolysis (Figure 6.5), we can further support the idea that the T_g is reduced by the increasing molecular weight of the acetal side chains. For the mixed acetal polymers (i.e. PVHN and PVHN9), there is high heterogeneity on the sample that does not allow the formation of a clear T_g gradient in

the DSC curves. Therefore, it is not possible to determine the T_g value for these polymer samples.

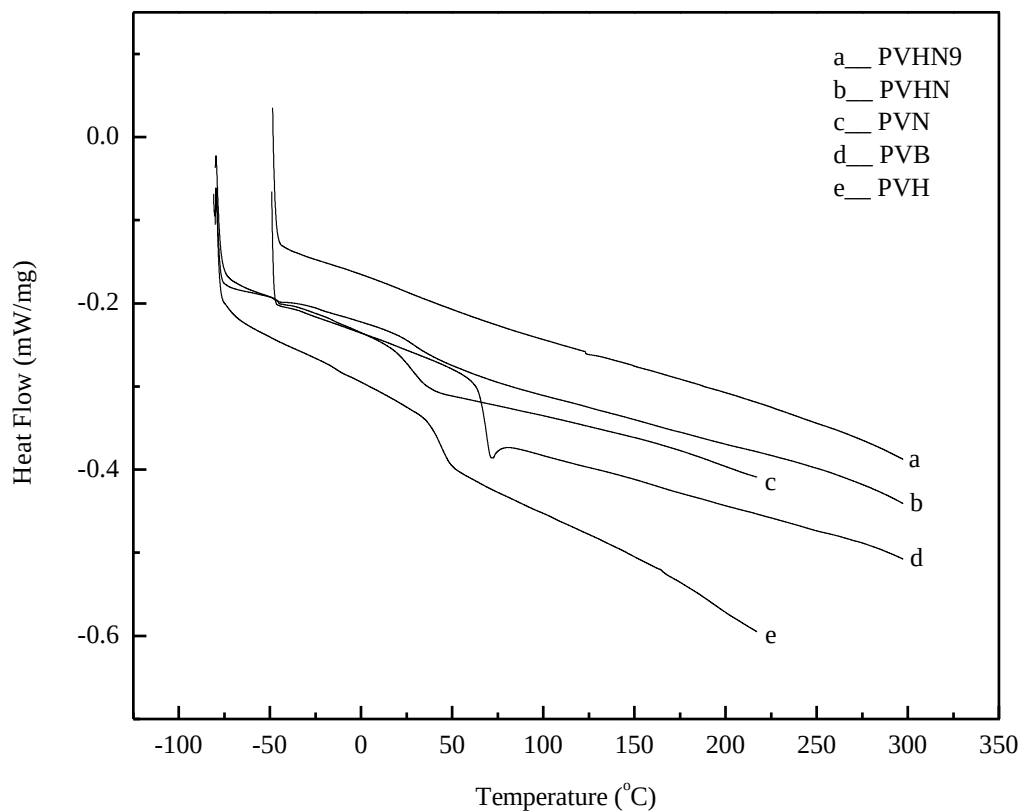


Figure 6.5 DSC spectra of polyvinyl acetals. PVB: polyvinyl butyral provided by Kuraray; PVH: polyvinyl alcohol reacted with hexanal based on stoichiometry; PVN: polyvinyl alcohol reacted with nonanal based on stoichiometry; PVHN: polyvinyl alcohol reacted with hexanal and nonanal (molar ratio 1:1) based on stoichiometry; PVHN9: polyvinyl alcohol reacted with hexanal and 9-oxononanoate (molar ratio 1:1) based on stoichiometry.

6.3.3 Gel permeation chromatography (GPC) for molecular weight measurement

The GPC analysis of PVH made in aqueous and organic solutions are compared in Figure 6.6 and the specific properties of both polymers are listed in Table 6.1. From these results, PVH prepared in aqueous reaction has a higher average molecular weight and a higher polydispersity index (PDI) value. This means that both the average molecular weight and the range of degrees of polymerization present in the sample are higher for PVH produced in water. The higher average weight molecular weight (M_w) and average number molecular weight (M_n) of PVH made in aqueous solution could be caused by the fact that in water solution, once the polymer is formed, the product separates from the aqueous phase immediately as solid, and in this way the reaction would be driven to the direction towards forming the polymer. However, in organic solvent the polymer is always dissolved in the same phase and thus the forward reaction encounters more resistance from the reverse reaction during PVH production. The higher PDI value may result from the same fact that the product separates from the reactants after being formed, which provides less chance for the polymer to structure regularly. The M_n value for both of the two PVH products is comparable to the highest reported M_n for PVB (around 100,000) in the Kuraray PVB Brochure [115].

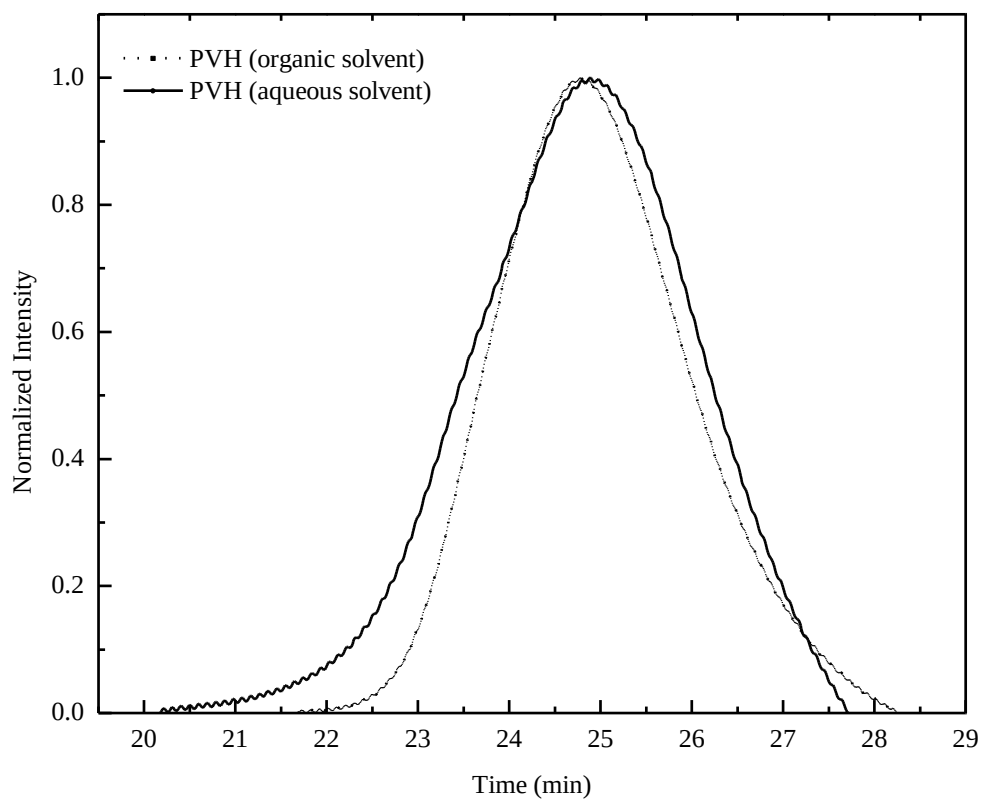


Figure 6.6 GPC spectrum of PVH made in two different solvents.

Table 6.1 Average molar mass of PVH made in two different solvents

Name	PVH (aqueous solvent)	PVH (organic solvent)
M _w	212,522	170,734
M _n	123,955	114,919
PDI	1.71	1.48

6.3.4 ¹H NMR analysis for PVH prepared in aqueous solution

NMR analysis was performed on the PVH polymer to elucidate its structure and degree of acetalization. The PVH used in this study was produced in organic solvent, as it was

organic solvents were superior to the commercially available PVB. When higher molecular weight aldehydes were used in the polymerization reaction, the decomposition temperatures reduced significantly, as in the case of PVN. Also, by mixing various aldehydes with different molecular weights, the thermal stability of the polymers was further reduced, as observed for PVHN and PVHN9. From the perspective of vinyl acetal polymer production, the utilization of hexanal seems more suitable for commercialization. Our studies revealed that synthesis of PVH using stoichiometric ratios of hexanal and PVOH is the most suitable for better thermal stability of the product. PVH synthesis in water with twice the stoichiometric amount of hexanal to PVOH showed that excess aldehyde entrapped in the polymer matrix was not easily removed and affected the thermal stability of the overall product. When the amount of hexanal was reduced to half of the stoichiometric ratio to PVOH, the thermal stability of the product was reduced due to heterogeneity in the sample.

DSC analysis showed that PVH has a lower T_g than the commercial polyvinyl acetal PVB. Also, this analysis revealed that higher molecular weight acetal groups reduce the T_g value of polyvinyl acetals.

The molecular weight distribution of PVH was determined by GPC and showed that the polymer produced in water contains a higher average molecular weight and a higher PDI than the same polymer produced in organic solvent. This difference may be related to the fact that the PVH falls out of solution when produced in water, driving the reaction to polymerization, but also allowing the product to be less regular. PVH formed in solvent was further analyzed by ¹H NMR to elucidate the structure of the polymer and also determine the level of acetalization. Our results agree to the structure of the targeted PVH

product and showed a degree of acetalization of 76.5% which is comparable to the commercial product of PVB.

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